PORTLAND HARBOR RI/FS

REMEDIAL INVESTIGATION REPORT

APPENDIX E
LOADING, FATE, AND TRANSPORT SUPPORTING INFORMATION AND CALCULATIONS

DRAFT FINAL

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E1.0 INTRODUCTION

This appendix presents the calculations performed to estimate current loading, fate, and transport terms as part of the Portland Harbor Remedial Investigation (RI).[1] Specifically, estimates for the following current loading terms are presented in this appendix:

- Upstream surface water

- Stormwater runoff

- Permitted discharges (non-stormwater)

- Atmospheric deposition

- Upland groundwater plumes

- Advective transport from subsurface sediment

- Advective transport from surface sediment.

In addition to these mass loading/transfer estimates, supporting items in this appendix include:

- Attachment E-1: Stormwater Loading Preliminary Data Analysis Steps

- Attachment E-2: Memorandum on Portland Harbor Stormwater Runoff Modeling (City of Portland 2008, pers. comm.)

- Attachment E-3: Data table of available upland soils chemistry

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[1] The focus of this analysis is on current loading terms to the study area and current in-river fate and transport processes. It is recognized that each loading term has a corresponding historical component that may be significant to the study area; however, insufficient quantitative data are available to support estimates of these historical terms.

E2.0 UPSTREAM SURFACE WATER LOADING ESTIMATES

The mass loading of the surface water loading contaminants (Table 6.0-1) was estimated using a quantitative approach based on empirical data. The purpose of this analysis was to estimate the dissolved and suspended contaminant mass flux entering via surface water at the upstream (river mile [RM] 11.8) end of the study area. Additionally, the annual surface water contaminant mass fluxes were estimated at sample transects located upstream of the study area (RM 16) and within the study area (RM 11, RM 6.3, and RM 4). The mass flux leaving the study area through Multnomah Channel (RM 3) and at the downstream end of the study area (RM 2) was also estimated. This appendix section presents the detailed steps taken to generate these loading estimates, from data sources and data treatment to the calculation approach. This section also presents the complete loading results.

E2.1 DATA SOURCES

Estimates of surface water loads entering the study area at the upstream (RM 11.8) boundary were based on Round 2A and 3A surface water contaminant concentration data from RM 16 and 11 (the two nearest sampling transects), and U.S. Geological Survey (USGS) flow information from RM 12.8 (Morrison Bridge Station 14211720). In addition to upstream loading evaluations, surface water loads were also calculated for transects located at RM 6.3 and RM 4. The mass flux leaving the study area through Multnomah Channel (RM 3) and at the downstream end of the study area (RM 2) was also estimated. Three surface water sampling events from the Round 2 sampling effort and four surface water sampling events from the Round 3 sampling effort provided the analytical data for the surface water loading calculations:

- November 2004 (Round 2A, Low Flow)

- March 2005 (Round 2A, Low Flow)

- July 2005 (Round 2A, Low Flow)

- January 2006 (Round 3A, High Flow)

- September 2006 (Round 3A, Low Flow)

- November 2006 (Round 3A, Stormwater-Influenced Low Flow)

- January/February 2007 (Round 3A, High Flow[2])

As noted in the list above, three types of sampling events were targeted: low river flow rate (low flow; <50,000 cubic feet per second [cfs]), high river flow rate (high flow; >50,000 cfs), and stormwater influenced (stormwater; sampling during low flow conditions with active runoff in the study area). Overall, the sampling events were

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[2] The January 2007 high-flow event involved sampling at only three stations (W023M, W024, and W025M) due to an unexpected change in flow conditions; therefore, the sampling event was restarted in February 2007. Results from both of those sampling events are included in this event data set.

distributed over the average water year, capturing the range of flow conditions, including base flow, rising limb, peak flow, and falling limb conditions (see Figure 5.4-1). The surface water sampling events are discussed in Section 2.1.3.1.4 and 2.1.4.1.1 of the RI report, and sampling locations are shown in Map 2.1-18. Also in the RI report, Section 5.4.1 and Tables 5.4-1 through 5.4-5 summarize sampling methods specific to each transect location and sampling event.

The RI data set and data summation methods were used in surface water loading calculations. Section 2 details the RI data set and data treatment, and the full RI data set for surface water for all sampled contaminants is presented in the site characterization and risk assessment (SCRA) database (Appendix A3).

Loading estimates were calculated for total, particulate, and dissolved phases for all surface water contaminants. The contaminant list is presented in Table 6.0-1. Particulate and dissolved contaminant concentrations measured in surface water with the XAD column sample collection technique were used for all volatile organic compound (VOC), pesticide, polychlorinated biphenyl (PCB), polychlorinated dibenzo-p-dioxin/furan (PCDD/F), and polycyclic aromatic hydrocarbon (PAH) loading calculations. Total concentrations were derived from the sum of the particulate and dissolved concentrations. Samples for total and dissolved metal analysis were collected using a peristaltic pump sampling method. Particulate metal concentrations were derived as the difference between the total and dissolved concentrations. Bis(2-ethylhexyl)phthalate (BEHP) was sampled with either XAD or peristaltic pump techniques in different sampling events. Where available, XAD data were used. Peristaltic BEHP data was used in all other cases. Results below detection limits were assigned a concentration of zero for the loading calculations prior to calculation of contaminant total concentrations (XAD), particulate concentrations (peristaltic), or transect data averaging.

Average discharge rates (recorded as cfs) for transects located at RM 16, 11, 6.3, and 4 for each event are based on 30-minute measurements collected by the USGS at the stream flow gauging station located at the Morrison Bridge at RM 12.8 (Station 14211720) (USGS 2008).[3] Because of the complicating influence of water from the Columbia River on Willamette River flow volume and direction at the RM 2 and Multnomah Channel transect locations (described in Section 5.4), average discharge rates were obtained from hydrodynamic modeling of the Willamette River performed by WEST Consultants (WEST 2006).

E2.2   APPROACH

The flow rate data and analytical data described above were used to estimate annual surface water mass loading to the study area at RM 11.8 (combined RM 16 and 11 data

[3] The flow rate values presented here are daily mean stream flow measurements from the USGS National Water Information System, www.waterdata.usgs.gov. These values were taken from the USGS Web site on June 16, 2008, and are considered to be draft and subject to change by USGS, which may refine ratings and calculations as needed.

sets) and at individual transects both upstream and within the study area (RM 16, 11, 6.3, and 4), and leaving the study area (Multnomah Channel and RM 2). As a first step, the average annual hydrograph (based on the 28-year period of record hydrograph record from 1975 through 2003) for the study area was divided based on a 50,000 cfs threshold into high-flow and low-flow portions. This step is described in detail in the following subsection (E2.2.1). Next, the surface water analytical data set was used to generate estimated concentration ranges for high-flow and low-flow conditions for each transect. This step is described in detail in section E2.2.2. Annual loads for high-flow and low-flow portions of the hydrograph were then estimated as the product of the concentrations and the flow rate. The annual mass loading estimates were generated by adding the fractional loading contributions estimated for high-flow and low-flow conditions for the year:

> Annual surface water contaminant load (kg/yr) = high-flow contaminant load (kg/yr) + low-flow contaminant load (kg/yr).

To express the uncertainty in these estimates, a range of annual loading was calculated based on the ranges in concentration for each contaminant. These ranges are presented in terms of lower, central, and upper annual loading estimates. Loading estimates and ranges were generated for each contaminant for total, dissolved, and particulate fractions. To illuminate any seasonal differences in surface water loading, ranges of loading estimates were also compiled for each contaminant evaluated and each transect for high-flow and low-flow river conditions.

E2.2.1 Surface Water Flow Rates

For the loading estimate calculations for RM 16, 11, 6.3, and 4, estimates of the average annual volume of water entering the study area during high-flow and low-flow periods were needed. To estimate these values, recent daily flow records (2004 through 2006[4]) and the 28-year average hydrograph (1975–2003) were evaluated. The daily records for these hydrographs were categorized as high flow (>50,000 cfs) or low flow (<50,000 cfs). (Note that the November 2006 stormwater-influenced low-flow sampling event was considered a low-flow event for this loading analysis.) For each hydrograph, the total annual high-flow volume was calculated as the sum of each individual daily flow with a volume greater than 50,000 cfs. Similarly, the total annual low-flow volume for each annual hydrograph was calculated as the sum of each individual daily flow with a volume less than 50,000 cfs. The high-flow and low-flow annual volume totals were divided by the total annual volume to determine the fraction of the total volume that can be attributed to high- or low-flow conditions for each year. Total flow volumes and high-flow:low-flow volume fractions for the individual years and the 28-year average are presented in Table E2-1. Because the data sets compared well, the 28-year hydrograph was considered adequately representative for use as the basis for defining the high-flow:low-flow volume ratio for a typical year. Fifty-two percent of the total annual

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[4] Daily flow data from October 1, 2007 –December 1, 2007 were not available; therefore, 2007 annual volume totals and high-flow:low-flow volume fractions were not calculated.

volume occurred during high-flow conditions and 48 percent during low-flow conditions, for a volume ratio of 1.07. The average annual duration of the low-flow period is 268 days, while high flows occur for a much shorter period of 98 days.

The Round 2A and 3A surface water sampling events and daily hydrograph data for the years characterized by those events (2004 through 2007) are presented in the RI report Figures 5.4-2a-d. Surface water sampling events superimposed on the 36-year average annual hydrograph are presented in the RI report Figure 5.4-1.

Due to the complicating influence of water from the Columbia River on river flow volume and direction in the lower reaches of the Willamette River (described in Section 5.4), the total annual flows used in loading estimates for the transects at Multnomah Channel (RM 3) and RM 2 were based on hydrodynamic model results (WEST 2006). These results quantify the distribution of the Willamette River flow volume between the main river channel and Multnomah Channel. Based on the model results, three flow conditions are typically observed in the Columbia/Willamette River system during the water year:

- Columbia River and Willamette River at low flow: Multnomah Channel carries up to 60 percent of the Willamette River flow

- Columbia River at low flow, Willamette River at high flow: Multnomah Channel carries 30 percent of the Willamette River flow

- Columbia River at high flow, Willamette River at low flow: Multnomah Channel carries 100 percent of the Willamette River flow, plus some flow from the Columbia River.

To determine river flow volumes from model outputs for use in loading calculations, daily average flow velocities were calculated from model outputs for each transect: RM 4[5] flow was calculated as the sum of the flow in model cells 35, 36, and 37 in the northerly direction; Multnomah Channel flow was calculated as the sum of the flow in the westerly direction for model cell 38; and RM 2 flow was calculated as the sum of the flow in model cells 39, 40, and 41 in the northerly direction. To determine the typical daily flow volume at each transect, the average daily flux rate (in units of cubic meters per second) for the years 2003 through 2007 was calculated, then multiplied by the number of seconds in a day. The annual flow volume for each transect was estimated by summing the individual daily average flow volumes.

The calculation of flow rates and volumes under the first two Columbia/Willamette flow conditions listed above is straightforward—the flow of the Willamette estimated at RM 4 is assigned to the main stem and Multnomah Channel at the appropriate ratios (40 percent and 60 percent, respectively, for conditions of low flow in both rivers; 70 percent and 30

[5] Modeled flows for RM 4 were evaluated to support estimation of flows at RM 2 and Multnomah Channel, as well as for comparison to flows measured at the USGS Morrison Bridge gauge at RM 12.8. Load estimates at RM 4 were calculated using the USGS Morrison Bridge data.

percent, respectively, when the Willamette River is at high flow relative to the Columbia). Under the last flow condition, when the Columbia River stage is higher than that of the Willamette River, some amount of Columbia River flow travels up the Willamette River main channel, mixing with Willamette River water and discharging through Multnomah Channel. Under conditions when Columbia River water travels upstream all the way to RM 2, modeled flow velocity results for the RM 2 transect are negative, indicating a flow direction reversal. During periods of flow reversal at RM 2, the Willamette River flow volume at RM 2 was assumed to be zero and all Willamette River flow (plus some Columbia River flow) was assumed to leave the study area through Multnomah Channel.

Hydrodynamic model results spanning the period from January 1, 2003 through December 31, 2007 were utilized. This time period encompasses the surface water sampling events (November 2004 through February 2007). Average annual hydrographs generated from model results are presented in Figures 5.4-3 and 5.4-4. The average annual hydrograph for RM 4 produced using the model results was found to be consistent with the 28-year annual average hydrograph measured at the USGS Morrison Bridge gauge at RM 12.8. No flow reversal was observed at RM 4.

For loading calculations, periods of low flow (<50,000 cfs) and high flow (>50,000 cfs) in the Willamette River were assigned to the RM 2 and Multnomah Channel transect data based on the daily flow records from the 28-year hydrograph of Morrison Bridge flows. Therefore, the same dates that met the conditions for high flow or low flow at upriver transects (RM 16, RM 11, RM 6.3, and RM 4) were assigned as high flow or low flow for RM 2 and Multnomah Channel, regardless of the actual flow volume estimated at those transects on a particular date. This approach was taken in order to take into account the relative Willamette River flow volume at RM 2 and Multnomah Channel separate from the flows associated with the Columbia River. This allowed a consistent attribution of concentration data for all transects.

During periods of flow reversal at RM 2, it is assumed that all of the Willamette River is discharging through Multnomah Channel, along with some water from the Columbia River. Therefore, if a sampling event occurred during a period of backflow, the measured concentrations would be affected by the mixing of Willamette and Columbia Rivers. The dates of surface water sampling events were compared to the hydrodynamic model results for actual (not average) years. This comparison indicated that none of the sampling events at Multnomah Channel or RM 2 occurred during a period of Columbia River backflow at RM 2. Based on this, it is reasonable to assume that the analytical concentration data used in loading calculations were not influenced by mixing with Columbia River water. The loading analysis is only concerned with the mass flux of contaminants leaving the study area. This allows the discharge of Columbia River water down Multnomah Channel to be ignored, simplifying the calculations of loading at the Multnomah Channel transect.

E2.2.2   Surface Water Average Concentration Calculation

This section describes the treatment of contaminant concentration data in support of the loading analyses, including data reduction for defining the upstream boundary of the study area and average concentration calculation.

Transect surface water samples involve vertically integrated sample composites collected from multiple lateral substations across the width of the river channel. Transect sampling is designed to estimate integrated water concentration through a cross section of the river or fraction of a cross section at a point in time. The transect sample concentration data used in the loading calculations comprise three different sample collection techniques:

- Equal Discharge Increment Sampling – Samples were vertically and horizontally integrated over the entire cross section of the river. These samples were collected at RM 11, 6.3, and 4 during Round 2A.

- Vertically Integrated: East-Middle-West Sampling – The cross-river transect was sampled at three discreet points: east bank, middle, and west bank. Each east, middle, and west sample is vertically composited over the depth of the river. These samples were collected at RM 11 and RM 2 during Round 3A.

- Near-Bottom/Near-Surface Sampling – Samples were collected from two vertical points in the water column and integrated horizontally across the width of the river transect. The near bottom sample was collected at a depth of 1 ft off the river bottom. The near surface sample was collected 3 ft below the surface. These samples were collected at RM 16, 6.3, 4, and Multnomah Channel during Round 3A.

Multiple sampling events were conducted between 2004 and 2007 under both low-flow and high-flow river conditions. For the loading estimates, it was necessary to generate concentration values representative of high-flow and low-flow conditions. These representative concentrations were calculated by separately averaging the individual sample concentrations that were collected during high-flow or low-flow conditions for each transect. For those locations where field replicate samples were collected, the individual discreet replicate/normal sample pairs, or east, middle, west sample triplicates, were averaged prior to the calculation of the high-flow or low-flow all-sample averages. Data points with concentrations below analytical detection limits were set equal to zero prior to averaging, consistent with the treatment of detection limits applied to all loading calculations.

A minimum, mean, and maximum concentration value were identified for each transect for high-flow and low-flow conditions from the corresponding set of averaged results (averaged to one value per transect per sampling event). These minimum, mean, and maximum values were applied to generate the ranges of lower, central, and upper surface water loading estimates for high-flow and low-flow conditions.

E2.2.2.1   Upstream Surface Water Average Concentration Calculation

Contaminant loading to the site via upstream (RM 11.8) surface water was estimated by combining the RM 16 and 11 contaminant concentration data sets to determine representative high-flow and low-flow minimum, mean, and maximum contaminant concentrations entering the study area. To assess whether the RM 16 and 11 data sets for each contaminant represented the same population of upstream data (in particular, whether the RM 11 data may be influenced by a source area between RM 16 and 11), a comprehensive graphical and statistical comparison of the contaminant data from both transects was conducted.

The RM 16 and 11 concentrations were analyzed on a chemical-by-chemical basis to determine the following:

- Concentrations to be combined for RM 16 and 11

- Concentrations to be combined for RM 16 and 11 following exclusion of outlying samples

- Concentrations to be evaluated separately for RM 16 and 11.

For each contaminant, the Mann-Whitney U-test was applied to compare the averaged RM 16 and 11 data sets. The Mann-Whitney U-test tests the null hypothesis that the two data sets were drawn from a single population. At a significance level of $\alpha = 0.05$, the null hypothesis was accepted for all of the contaminants, indicating that no statistically significant difference could be shown between the RM 16 and 11 data sets. The Mann-Whitney U-test results are presented in Table E2-2.

Figures E2-1 through E2-13 present bar charts of RM 16 and RM 11 contaminant concentrations for discreet sample concentration data and averaged concentrations. These charts were visually analyzed to identify high-concentration samples that were not likely to be representative of conditions upstream of the study area. In particular, samples collected at RM 11 east were scrutinized for elevated concentration values due to a potential contaminant source on the east bank of the river at RM 11.3, and best professional judgment was applied to identify those samples that exhibited notably higher concentrations than other RM 11 or RM 16 samples for a given analyte. These samples, which are identified in Table E2-3, were excluded from all upstream concentration calculations and loading estimates.

Table E2-4 presents the surface water data used in the individual loading estimates for each surface water transect (RM 16, 11, 6.3, 4, 3 and 2). Table E2-5 presents the data used to generate the upstream (RM 11.8) loading estimates. These tables present original sample data which has not been averaged. The high-concentration RM 11 samples identified in Table E2-3 have been excluded from upstream loading calculations, and therefore are not presented in Table E2-5. These samples are included in the individual river mile loading estimates and Table E2-4.

E2.3   SURFACE WATER LOADING RESULTS

Based on the calculations described above, loading estimates for each surface water contaminant were generated for the minimum, mean, and maximum concentrations for high-flow, low-flow, and total annual flow (high-flow plus low-flow) conditions for dissolved, particulate, and total concentration fractions. The complete results are presented in Table E2-6 (individual river miles) and Table E2-7 (upstream of the study area).

E2.4   UNCERTAINTY

Uncertainty associated with the surface water loading estimates is related primarily to the adequacy and representativeness of the analytical data set. The data sets are derived from grab samples, not time-weighted composites. Further, a limited number of samples were collected under a limited number of flow conditions. This prohibits a thorough understanding of temporal and flow variability in surface water quality, and is an important source of uncertainty of unknown magnitude. Another source of uncertainty is associated with the use of modeled flow data for the RM 2 and Multnomah Channel loading results.

Compared to other loading terms, the surface water loading estimates are considered to be reasonably good estimates of the typical current annual loads, with lower uncertainty relative to other loading term estimates, considering the use of empirical site data in all calculation steps, the advanced sampling techniques applied in data collection, and the consistent patterns in the data sets by event type.

The concentration range observed among the sampling events is the only direct insight available into the uncertainty associated with this approach. Sediment trap data provide some additional perspective into the suspended solids loading estimates because they reflect longer sampling periods (four quarterly samples); however, for direct comparison, these samples are spatially limited (not representative of the entire transect) and mechanism-limited (not necessarily likely to equally capture particles of all sizes). The sediment trap results are discussed in comparison to surface water suspended solids in the following section.

E2.4.1   Comparison of Sediment Trap Data to Surface Water Suspended Solids

Sediment trap data were collected in 16 locations over four consecutive quarters (see Section 5.3 for details). Each of these data sets represents continuous measurement of suspended solids over the sampling period, at a near-bottom point in the river, which is in contrast to the event-specific snapshot record represented by the surface water suspended solids data set. While the sediment trap data are not directly comparable to the measurements of surface water suspended solids concentrations, it is worthwhile to compare the findings and look for trends that could inform uncertainty in the surface water suspended solids loading estimates. The sediment trap samples also differ from the surface water suspended solids data because the sediment trap data represent the record

for a single near-bottom point in space in the river, as opposed to the vertically and horizontally integrated surface water sample transects. Additionally, it is conceivable that the some of the finer grained and/or less dense suspended solids measured in surface water might not be captured in the sediment traps.

To inform the loading analysis, sediment trap data from RM 15 to 1.8 were plotted with all of the surface water transect data for high-flow and low-flow events for physical parameters and Aroclors, TCDD TEQ, DDx, and total PAHs.

Mass and fraction of organic carbon (f_{oc})[6] in the sediment trap and surface water data sets were compared to evaluate physical characteristics. Because sediment traps do not quantify the mass of sediments moving through the river, direct comparison of mass loading estimates was not possible. Instead, the sediment accumulation rates (mass/area/time) were plotted against total suspended solids (TSS) values using a double y-axis plot. This plot, Figure E2-14 (upper plot), shows that the highest accumulation rates across the plotted range correspond to the first quarter of sediment trap sampling, which was the period of highest flow during the sampled year. This is consistent with the observed higher TSS values in the highest flow surface water samples. The records do not agree as well in comparison of f_{oc} results (Figure E2-14, lower plot). The sediment trap data show a fairly narrow range of observed f_{oc} values (1.1 to 3.5 percent); however, the surface water suspended solids data shows a much larger range (0 to 30 percent). In particular, higher f_{oc} values for TSS are apparent for low-flow conditions at transects at RM 11 and 6.3; similar high values are not observed in the sediment trap data set. These differences might reflect more variability in detrital organic carbon loads in the surface water TSS fraction than in materials captured by the sediment traps. Alternately, they might illustrate the difference in the limited spatial representativeness of the sediment trap samples as compared to the surface water transects. Finally, these values could reflect the uncertainty in the surface water estimate of f_{oc} for cases where TSS values were very low or below detection limits. For this estimate, variability in TSS values may result in relatively large variability in the calculated f_{oc} value.

Sediment trap and surface water data sets, and transect surface water particulate concentrations were compared to the sediment trap solids dry weight concentrations for PCB congeners, TCDD TEQ, DDx, and total PAHs (Figures E2-15 through E2-18). Total PCB congeners (Figure E2-15) surface water TSS and sediment trap data concentration ranges are comparable, with the exception of two elevated sediment trap concentrations at RM 11 (ST007). The sediment trap samples at RM 11 were taken near a suspected PCB source. Thus, these results may be biased high relative to the nearby surface water transect TSS samples. During periods of higher flow (Q1 and Q2), the

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[6] f_{oc} was not analyzed in surface water TSS samples; therefore, the f_{oc} for each TSS sample was calculated as the difference of the surface water total organic carbon (TOC) and the dissolved organic carbon (DOC), all divided by total suspended solids, such that $f_{oc} = (TOC - DOC)/TSS$. For f_{oc} calculations, non-detect values were set equal to one-half detection limits. Additionally, if DOC > TOC, the f_{oc} was set equal to 0.

sediment trap samples from that location do not show such a strong signal from the local source.

TCDD TEQ sediment trap sample results (Figure E2-16) show generally larger ranges of solids concentrations than the corresponding proximal surface water TSS samples. The exception to this is found around RM 16, where the range of sediment trap concentrations and surface water concentrations are comparable.

DDx results (Figure E2-17) show good comparability of sediment trap and surface water TSS concentration ranges along the river, with the exception of the lowest flow sediment trap sample (Q4) at RM 11.3, which is elevated relative to the surface water transect range. Again, this may reflect a local source area influencing the sediment trap samples during low-flow conditions.

The total PAHs comparison (Figure E2-18) indicates that the surface water TSS concentration range is generally larger than the associated proximal sediment trap concentration range. The exception to this for PAHs is found at RM 6 (ST005), where several elevated sediment trap sample results (the highest of which is from the lowest flow period, Q4) are higher in concentration than the surface water TSS results at RM 6.3. This likely reflects the influence of the known PAH source areas near ST005.

In summary, comparison of the sediment trap and surface water TSS data indicate that the surface water TSS data reasonably approximate the longer-term sediment concentrations provided by the sediment traps, in spite of the snapshot nature of the surface water samples. While several sediment traps show higher contaminant concentration ranges due to proximity to known source areas, the surface water TSS data generally show comparable-to-higher ranges of concentrations. Because the surface water loading estimates present results in terms of these concentration ranges, it is expected that the estimates are reasonable representations of a full year of conditions.

E3.0 STORMWATER LOADING ESTIMATES

This section presents the methods for conducting stormwater loading estimate calculations using stormwater composite water and sediment trap data.

E3.1 OVERALL LOADING METHODS

The stormwater sampling location rationale was designed in accordance with a commonly used approach of applying "representative" estimates of stormwater contaminant concentrations for various land use types (Schueler 1987). A land-use-based contaminant load modeling approach was used to estimate loads across the entire study area. Contaminant loading models use site characteristics (land use and percent impervious area) and land-use-specific loading rates to estimate overall loading into the receiving waters. This approach has been modified to better fit the unique data needs and land use characteristics of the study area, as well as the practical constraints for this sampling effort.

E3.1.1 Estimation of Long-Term Loads

Ideally, estimation of long-term loads would involve a large number of samples taken over the course of many years and from many types of storms, pollutant sources, and runoff conditions. Instead, both stormwater composite water chemistry samples and sediment trap chemistry samples were collected at the locations discussed in Section E3.4 of this appendix. These two measurements provide data to support two independent means of estimating stormwater contaminant loads as explained below in Sections E3.5.1 and E3.5.2.

It is anticipated that these two methods (composite water and sediment traps) will result in different predictions of mass loading at most locations. It is beneficial to estimate loads via two independent methods because each method has intrinsic measurement artifacts that lead to differing load estimates. The advantages and disadvantages of each method are to some extent complementary. By using two approaches, the disadvantages of each method can be better understood and the two loading estimates provide a better overall sense of the potential range of contaminant loads.

E3.2 DATA SOURCES

The stormwater composite water and sediment trap data were collected in accordance with the Round 3A Stormwater FSP and Addendum (Anchor and Integral 2007a, 2007b) and the Round 3A SSR (Anchor and Integral 2007c), and analyzed in accordance with the Quality Assurance Project Plan Addendum 8 (Integral 2007). The field sampling activities are described in detail in the Round 3A Upload Stormwater Sampling Field Sampling Report (FSR; Anchor and Integral 2007d) and the FSR Addendum (Anchor and Integral 2008). Data were collected during a total of 15 storm events, with each outfall sampled an average of three times. Sediment traps were left in place for 3 to 7 months during two separate sampling periods. Due to the limited time span of sample collection

and the known variability of stormwater, this data should be considered to represent a snap shot of stormwater entering the study area during the sampling period.

Samples from three general categories of land use locations were included to obtain a practicable and sufficient data set. Samples were collected from a subset of drainage basins/outfalls within each category in the study area. These locations were sampled by the LWG and Port of Portland (Terminal 4) during two sampling efforts in the spring/summer of 2007 (Round 3A) and the fall/winter of 2007–2008 (Round 3B). One additional site (GE Decommissioning) was sampled by GE during the same time frame. Results from the GE investigation are included in the overall LWG stormwater data set. In early 2008, the City of Portland collected three additional samples to supplement the residential data set, and these samples are included as well. The three categories of locations are:

- **Representative Land Use Locations.** Twelve locations were selected as representative of five land uses (based on zoning) within the overall drainage area. These land use types are as follows:[7]

  – Residential land use (two locations) representing approximately 8 percent of the overall drainage basin to the study area

  – Major transportation corridors (two locations) representing approximately 2 percent of the basin

  – Heavy industrial land use (five locations) representing approximately 25 percent of the basin

  – Light industrial land use (four locations) representing approximately 8 percent of the basin

  – Parks/open space land use (one location) representing approximately 57 percent of the basin

- **Specific (Non-Representative) Industrial Locations.** Fifteen industrial locations were selected with potentially non-representative contaminant sources that cannot be easily extrapolated from generalized land use measurements.

- **Multiple Land Use Locations.** Two locations were selected to directly measure stormwater discharge from relatively large basins that have a mixture of land use zones to provide a cross-check with land use loading estimates. Additionally, during the first round of sampling, the Highway 30 location was inadvertently sampled in a location that included runoff from both highway and industrial areas. The samples from this location were renamed as "Yeon Mixed Use" and will also be used as a cross-check for land use loading estimates as further discussed in Section E3.7.2.

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[7] Another kind of land use commonly evaluated in stormwater investigations is the "commercial" category, but this is a very minor use (less than 1 percent) within the overall drainage and was judged not to warrant a specific sampling location. Data from the residential land use type was used for commercial land use areas.

E3.2.1   Database Development and Rules

There were several deviations from the SCRA database rules for the stormwater data set, based on agreements made by the Stormwater Technical Team to include all results, including laboratory replicates and field duplicate results, in the stormwater project database. All laboratory replicate and field duplicate results were included. A detailed summary of how laboratory replicate and field duplicates were treated is included in Attachment E-1. The RI data summation methods (as described in Section 2) were used in stormwater loading calculations. Once the LWG database was prepared, it was queried to reduce it to a "working database" to include only those contaminants in Table 6.0-1.

E3.2.2   Reclassification Analysis

Prior to conducting loading calculations, the data set was evaluated in order to determine whether or not *a priori* assumptions about representative land use locations versus non-representative land use locations were correct. A detailed summary of how this reclassification analysis was conducted is included in Attachment E-1.

The reclassification analysis resulted in many locations being reclassified from non-representative to representative and a smaller number of locations being reclassified from representative to non-representative. Summary statistics on the stormwater data were compiled after this reclassification analysis was completed. A summary of the non-representative locations for each contaminant is included in Table E3-1.

Several locations were reclassified as non-representative solely on the basis of outlier non-detect values. These locations are listed in Table E3-1 for reference and also shown in Maps 4.4-1a–d, but the non-representative loading rates from these sites were not included in the calculation of total loads; instead the "representative" land use loading rate was applied. These locations and corresponding contaminants include:

- Schnitzer WR-384: PCB 169

- GE Decommissioning Facility: arsenic

- Arkema WR-96: dieldrin and total chlordanes

- OF-22B: 4,4´-DDT and gamma-hexachlorocyclohexane (Lindane).

E3.3   APPROACH

The stormwater composite water and sediment trap data described above were used to estimate annual stormwater mass loading rates to each Fate and Transport Model cell within the study area.

E3.3.1   Stormwater Composite Sample Approach

As a first step, the stormwater analytical data set was used to generate estimated concentration ranges for each land use and "non-representative" site, as shown in

Table E3-2. The specific details of these calculations are included in Attachment E-1. Next, the stormwater runoff volumes draining to each Fate and Transport Model cell were calculated for each land use and "non-representative" location using the City of Portland's GRID model as summarized in Section E3.5.3 below and as described in detail in Attachment E-2. Loads were then estimated as a product of the calculated concentration estimates and the flow rate from the 50th percentile flow year in order to estimate a central tendency. The annual mass loads were generated by adding the loading contributions from each land use and non-representative site for each Fate and Transport Model segment:

> Annual stormwater contaminant load (kg/yr) = heavy industrial stormwater contaminant load (kg/yr) + light industrial stormwater contaminant load (kg/yr) + residential stormwater contaminant load (kg/yr) + parks/open space stormwater contaminant load (kg/yr) + major transportation stormwater contaminant load (kg/yr) + "non-representative" site stormwater contaminant load (kg/yr)

To express the uncertainty in these estimates, a range of loading rates was calculated for each contaminant by multiplying the 50th percentile flow year runoff volumes by a range of concentration estimates, including the geometric mean, basin-weighted mean, 5th percentile, and 95th percentile. The basin-weighted mean was weighted using a unitless weighting factor for each sample location based on its runoff volume divided by the sum of all volumes for all locations within a particular land use.

Stormwater loads for pesticides were approached in a slightly different manner than loads for metals, PAHs, or PCBs due to a lack of representative composite water samples. Pesticides were only analyzed at a small subset of locations in composite water samples, but they were analyzed at nearly all locations in sediment trap samples.

Composite water samples collected from parks/open space or transportation land uses were not analyzed for pesticides; additionally, limited composite water samples from light industrial and residential land uses were analyzed for pesticides. However, a larger number of sediment trap samples from each of the aforementioned land uses was collected and analyzed for pesticides. In order to more accurately approximate the annual pesticide loads to the study area, sediment trap data and statistics were substituted for composite water statistics for light industrial, parks/open space, residential, and transportation land uses. This method was also used for non-representative locations that did not have composite water data (i.e., WR-147). The appropriate sediment trap data for a specific land use or non-representative location were multiplied by the geometric mean TSS value for the land use or location to obtain a surrogate composite water value. These surrogate composite water values were then used to calculate stormwater composite water loads to the study area.

E3.3.2   Stormwater Sediment Trap Sample Approach

The approach for stormwater sediment trap data is similar to the approach used for composite water. Before calculating an annual surface water contaminant load, the

contaminant solids load was calculated as the product of the sediment concentration and the geometric mean TSS concentration for a particular land use. The stormwater sediment trap contaminant solids concentrations are presented in Table E3-2.

Annual loads were then estimated as a product of the contaminant solids loading rate and the runoff volumes from the 50th percentile flow year. The annual mass loads were simply generated by adding the loading contributions from each land use and non-representative site for each Fate and Transport Model cell:

> Annual stormwater contaminant load (kg/yr) = heavy industrial stormwater contaminant load (kg/yr) + light industrial stormwater contaminant load (kg/yr) + residential stormwater contaminant load (kg/yr) + parks/open space stormwater contaminant load (kg/yr) + major transportation stormwater contaminant load (kg/yr) + non-representative site stormwater contaminant load (kg/yr).

To express the uncertainty in these estimates, a range of loading estimates was calculated for each contaminant by multiplying the runoff volume from the 50th percentile flow year by a range of contaminant solids loading estimates, including the geometric mean, basin-weighted mean, 5th percentile, and 95th percentile. The basin-weighted mean was weighted using a weighting factor for each sample location based on its runoff volume divided by the sum of all volumes for all locations within a particular land use.

For non-representative locations with sediment trap data that were either not collected (OF-22B) or unavailable due to sampling method inconsistencies (WR-96), composite water data were substituted in order to calculate a load from that location. In this case, composite water statistics were used as surrogate for sediment trap statistics. Surrogate sediment trap statistics were then used to calculate the stormwater sediment trap loads to the study area.

E3.3.3 Stormwater Flow Rates

As detailed in Attachment E-2, and summarized in this section, runoff volumes were calculated for each land use category and "non-representative" location by the City of Portland Bureau of Environmental Services using the GRID model.

E3.3.3.1 Description of GRID model

The GRID model is a geographic information system (GIS)-based reconnaissance-level pollutant model developed by the City of Portland Bureau of Environmental Services to calculate stormwater runoff volumes and TSS loading rates. The GRID model was used as a part of this stormwater loading calculations effort to provide flow volumes only.

Data compiled for each 100-ft by 100-ft grid cell includes precipitation, pervious/ impervious area, and zoning area (or land use). With these data, runoff volumes for various land use types are calculated using a series of equations known as the "Simple Method" developed by Schueler (1987).

The equation for runoff volume using the Simple Method is:

$$R = P * Pj * Rv$$

Where:

R = Annual runoff per unit area (cm/month)
P = Annual rainfall (cm)
Pj = Fraction of monthly rainfall events that produce runoff (usually 0.9)
Rv = Runoff coefficient (unitless).

The annual runoff per unit area was then converted to units of volume/month based on the depth of runoff times the area in question.

E3.3.3.2   Runoff Volumes

Runoff volumes were calculated, using the City of Portland Bureau of Environmental Service's GRID model. Runoff volumes were calculated for each land use Fate and Transport Model shoreline cell based on the GRID-model-determined watersheds draining to the corresponding segment of shoreline. Additionally, runoff volumes were calculated for each non-representative location listed in Table E3-1, as loads to the study area from these locations were input into the model separately since they were deemed to be non-representative through the data analysis explained in Attachment E-1. Additional discussion on calculating volumes from non-representative sites is also included in Attachment E-2.

Yearly runoff volumes were generated using rainfall records from 2002, which is the 50th percentile river flow year. The volumes for each land use and non-representative basin are summarized by Fate and Transport Model cell in Table E3-3. For reference, a summary of land use percentages by study area, Fate and Transport Model cell, and non-representative location is included in Table E3-4.

E3.4   STORMWATER LOADING RESULTS

As noted, the Portland Harbor study area is divided into five representative land use types based on zoning: heavy industrial, light industrial, open space, residential/commercial, and major transportation. Applied concentrations and runoff volumes by land use and non-representative locations are shown in Table E3-2 and Table E3-3, respectively.

Stormwater loading estimates for composite water and sediment trap data are presented in Tables E3-5a (composite) and E3-5b (sediment trap) by basin. Each basin corresponds to the Fate and Transport Model cell number. The annual loads were calculated using the applied concentrations and yearly runoff volumes as discussed in Section E3.5.2. For each analyte and basin, the load estimate geometric mean, basin-weighted mean, 95th percentile, and 5th percentile are presented in units of kilograms per year. The estimated annual loads to the study area are presented graphically on Maps E3-1a–b through E3-

32a–b. The same color ramping scale is used for both composite water and sediment trap maps so that comparisons between the two separate loading estimates can be made.

E3.5   UNCERTAINTY

The data evaluation in this section uses data generated for use in the Fate and Transport Model, and the scale of the loading assessment is therefore defined by the scale of the model input. The scale of the model cells is adequately refined spatially to support comparison of stormwater loading term estimates with estimates of other loading terms.

Data used to estimate the stormwater loads were collected during a total of 15 storm events, with each outfall sampled an average of three times. Sediment traps were left in place for 3 to 7 months during two separate sampling periods. Due to the limited time span of sampling and the known variability of stormwater, these data should be considered to represent a "snapshot" of stormwater entering the study area during the sampling period. ,

The methodology for calculating stormwater loading assumes that concentrations measured in individual sampled outfalls at non-representative sites are indicative of concentrations for all stormwater discharging from that upland site. This methodology has inherent uncertainty associated with it, as concentrations can vary significantly based on the physical characteristics of the drainage basins associated with stormwater discharges. For example, if a drainage basin that was sampled drains a known upland source area, the concentrations measured in this discharge will be significantly higher than stormwater discharges at the remainder of the upland site. Thus, this example will overestimate stormwater loading for this site.

The uncertainties associated with the runoff volume estimates from the City of Portland Bureau of Environmental Service's GRID model are discussed in Attachment E-2. Loads generated in this report are annual loads based on the 50th percentile river flow year.

E3.5.1   Records Excluded from Loading Analysis

Particular records were excluded from the working database due to various factors identified by the Stormwater Technical Team. These outfall locations are shown on the Stormwater Drainage Basin Characterization Maps 4.4-1a–d. The following data were not included per discussions with the Stormwater Technical Team:

- St. Johns Bridge (WR-510) – After the conclusion of Round 3A sampling, the Stormwater Technical Team discussed that the data from St. Johns Bridge may not be representative of long-term transportation loadings from general highway runoff because the bridge was recently repaired, repaved, and repainted. Therefore, a new location (Hwy 30B) was selected for sampling during Round 3B so there would still be two major transportation locations. These St. Johns Bridge data were not included in the loading calculations presented in the RI. However, since the major transportation land use represents only 2 percent of the study area,

the inclusion or exclusion of these data is not expected to greatly influence the loading estimates.

- Arkema WR-96 – Due to insufficient sediment volume collected in sediment traps through both rounds of sampling at WR-96, the Stormwater Technical Team suggested the use of sediment collected from within the outfall structure at this location for sediment sample analysis because there was a large amount of sediment accumulated around the sediment trap bottles. Because this sediment was collected differently from other sampling locations, the "non-representative" loading estimates based on sediment trap data from this site were not included in the loading calculations or discussed in Section 6 and Section 10. Instead, the loading estimate from the composite water data was used for this analysis.

E3.5.2   Comparison of Extrapolated to Measured Loads

As discussed, not all runoff within the study area was sampled. Rather, sites that were representative of general land use types were sampled and the data used to extrapolate to other locations, on a land use basis, where runoff was not directly sampled. To provide an estimate of overall uncertainty created by this method, load values obtained from actual samples at three basins with multiple land uses were compared to the range of calculated loads using the extrapolated land use load method.

These sampled multiple land use basins, as shown in Map 4.4-1c, include the following locations:

- OF-18 is an estimated 413-acre basin containing heavy industrial, residential, open space and major transportation (Hwy 30) land use.

- OF-19 is a 485-acre basin containing heavy industrial, open space, and major transportation land use.

- Yeon Mixed Use is an 18-acre sub-basin that drains to the river at OF-18. This basin includes major transportation land use and heavy industrial land use.

Extrapolated loads for each of these basins were calculated using generalized stormwater loading criteria for each land use developed from the stormwater data. For example, the stormwater loading in the Yeon Mixed Use basin could be calculated in two ways:

- Stormwater loading using measured concentrations:

$$L_{Yeon\ Mixed\ Use} = C_w\ x\ V$$

Where:

L = Load (kg/year)
C_w = Measured concentration (µg/L) for Yeon Mixed Use
V = Volume of discharge from land use for 50 percent flow year.

- Stormwater loading using extrapolated data:

$$L_{\text{Yeon Mixed Use}} = (C_w \times V)_{\text{heavy industrial}} + (C_w \times V)_{\text{major transportation}}$$

Where;

L   = Load (kg/year)
C_w = Concentration (µg/L) for particular land use
V   = Volume of discharge from land use for 50 percent flow year.

Total PAHs, total PCB congeners, DDx, BEHP, hexachlorobenzene, lead, and mercury were included in this comparative assessment.[8] Loads based on stormwater composite data and sediment trap data were evaluated. This assessment focused on whether the measured loading value was within the upper- and lower-bound range of calculated values (defined as the 95th and 5th percentiles, respectively) using the representative method; and the relative percent difference (RPD) of the measured load and mean representative calculated load. The RPD was calculated as the absolute difference between the measured and mean represented calculated load divided by the average:

$$RPD = \frac{\left| L_M - \bar{x}_C \right|}{\left(\left[L_M + \bar{x}_C \right] \big/ 2 \right)} \times 100$$

Where:

RPD = Relative percent difference
L_m = Measured load
x_c = Mean calculated load.

E3.5.2.1   OF-18 Segregation Evaluation

Prior to comparing measured to representative calculated loads for OF-18, an analysis was conducted on the effect of data segregation at this location as a result of the duplicate/replicate analysis performed on composite water data. As a result, nine results were flagged in the data set due to divergence between the normal and duplicate result. The effect of removing these samples on the measured load relative to the calculated loads was assessed to determine the overall effect on the measured load. Graphical comparison of the measured loading values, with and without the segregated data included, to the range of calculated loads was performed for BaP, lead, PCB-077, PCB-105, PCB-106/118, PCB-126, PCB-156/157, total PCB congeners, and total PCB congener (TEQ).

Results of the comparison of loads with and without segregated data to calculated loads for OF-18 are provided in Figure E3-1 and Table E3-6. The evaluation of the results

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[8] BEHP and hexachlorobenzene were included in the comparison for sediment trap based loads only.

without the segregated data resulted in lower measured loading values than the loads without the segregated data. Measured values for BaP and lead fell above the 95th percentile of the calculated loading values. For individual PCBs, total PCB congeners, and total PCB TEQ, the loading values using the unsegregated data fell within the range of calculated loads. Loads measured using the segregated data exceeded the upper-bound calculated load for two PCB congeners, as well as total PCB congeners. Based on this evaluation, the effect of segregating data for OF-18 reduced the loading estimates, tending to bring them more in line with calculated loading values. This method is also generally consistent with the methods used throughout this study to extrapolate load calculations. Therefore, the following discussion focuses on the analysis using segregated data.

E3.5.2.2   Results and Discussion

Results of the comparison between measured and calculated representative loads based on sediment trap data for OF-18, OF-19, and Yeon-NW35 are presented in Table E3-7. In general, measured loads were within the range of calculated loads and were reasonably close to estimates of central tendency. RPDs between measured and mean calculated loads were typically less than 100 percent. The greatest variability between measured and calculated loads was at OF-18. Measured loads greater than the 95th percentile calculated load and with an RPD exceeding 100 percent are mercury, total PCB congeners, DDx, BEHP, and hexachlorobenzene. Measured loads for mercury, lead, and BEHP are greater than the upper-bound estimate, with the RPD exceeding 100 percent at OF-19 on a dry-weight basis. However, measured loads were greater than the upper-bound estimate of calculated loads less than a factor of four. The measured loading estimate for total DDTs at OF-19 is less than the lower-bound estimate of the calculated load.

A comparison of calculated and measured loads using stormwater composite data at OF-18, OF-19, and Yeon-NW35 is provided in Table E3-8. Measured loads at OF-18wer greater than the upper-bound calculated load for lead, mercury, and PAHs; the RPD was greater than 100 percent for lead. The measured load for lead is greater than the calculated upper-bound load at OF-19, the RPD is 84 percent. Finally, the total PCB congeners (TEQ) measured load at Yeon-NW35 fell below the calculated lower-bound estimate and had an RPD exceeding 100 percent. Frequently, the range of calculated loads had a relatively small range (often less than a factor of 10), which may account for the measured loads exceeding upper-bound estimates but with relatively low RPDs. In general, measured loads were between the mean and upper-bound calculated loads, indicating reasonable agreement between the two methods of determining loads for mixed land use locations. Measured loads exceeded the upper-bound calculated loads by a factor of 2.5 or less. Overall, this comparison appears to indicate that the representative loads are a reasonable estimate of loads from larger mixed land use basins had they been measured in the same general time period. This indicates that the representative land use loading method is a reasonable method for estimating loads for the larger study area drainage basin.

E3.5.3   Processed Data versus Unprocessed Data

As part of the uncertainty analysis, the effect of data processing rules on the composite stormwater data set used for loading calculations was evaluated. Specifically, measures of central tendency (median) and upper-bound estimates (95th percentile) of stormwater analytes were compared on a land-use-specific basis using the final data set used for loading calculations discussed in this section and the unprocessed data that has not undergone any prior analysis. Processed data used in this analysis are summarized in Appendix E3.6, the unprocessed data are presented in Appendix C1. The rationale behind this comparison is that the implications associated with the data processing decisions relative to methods that contains no processing of data can be evaluated.

Table E3-9 provides a side-by-side comparison of processed and unprocessed data set summary statistics for used in loading calculations. In addition, the difference in number of samples in each data set and the percent difference for the mean, median, and 95th percentile were calculated. The percent difference (PD) was calculated as:

$$PD = \frac{\left(X_U - X_P\right)}{\left[\left(X_U + X_P\right)\middle/ 2\right]} \times 100$$

Where:

PD = percent difference
XU = value of unprocessed data set summary statistic (e.g., mean)
XP = value of processed data set summary statistic.

Scatter plots of paired unprocessed versus processed data median and 95th percentile values are presented on Figures E3-2 and E3-3, respectively. A line representing a 1:1 relationship (i.e., slope[m] = 1) is included on each graph. Ideally, if there were no differences between data sets, all points on these graphs would fall on this line (i.e., PD = 0). Points that lie to the right of the line indicate that the processed statistic value for that point exceeds the paired unprocessed statistic value (PD > 1), while points to the left indicate the unprocessed statistic value is greater (PD < 1).

E3.5.4   Results and Discussion

In general, differences between median values in the processed and unprocessed data sets were small. PDs did not exceed 200 percent and infrequently exceeded 100 percent. The greatest variability and highest PD values were observed for pesticides in the light industrial land use classification. These differences are primarily due to low sample count (n = 1 to 6) and the low frequency of detection (0 to 67 percent). Based on Figure E3-2, median values tended to cluster near the 1:1 trendline, indicating relatively low differences in median values. Values did occur more frequently to the right of the trendline, indicating that median values tended to be higher in the processed data set. Variability tends to increase at the lower end of the scatter plot, primarily due to pesticide

values near the detection limit and/or low sample counts for these analytes. Overall, differences are considered relatively low between median values in these data sets.

The 95th percentile values were generally larger for the unprocessed data set. All PD values were less than 200 percent, but values above 100 percent were more frequently observed than for the median statistic (Figure E3-3). The unprocessed 95th percentile typically exceeded the corresponding processed value, primarily due to the removal of outliers from the representative data set during the reclassification analysis of stormwater data.

The uncertainty associated with the stormwater processing on summary statistics for analyte values is considered relatively low, and appears to be lower than the uncertainty associated with the representative land use load calculation approach previously discussed. Therefore, the uncertainty s created by the individual processing steps appears to low.

E4.0 PERMITTED NON-STORMWATER POINT SOURCE DISCHARGE LOADING ESTIMATES

Point source permitted non-stormwater discharges to the river comprise another external loading term to the study area. This section presents the data sources, approach, and results of the semi-quantitative estimation of the annual mass load of contaminants to the system via this loading mechanism.

E4.1 DATA SOURCES

This loading analysis focused on National Pollutant Discharge Elimination System (NPDES)-permitted discharges from commercial, industrial, private, or municipal outfalls within the river mile range of the study area. Data compilation for this analysis involved identifying the list of active NPDES permit holders discharging to the study area, obtaining copies of those permits, and obtaining discharge monitoring records for those permits. Those activities and products are described in this section. Note that this analysis is specifically limited to permitted wastewater discharges to the study area and does not represent stormwater discharges or other types of point sources.

DEQ issues general and individual NPDES permits. General permits are issued to dischargers with operations and waste streams that fit into categories that can be regulated with a standard set of monitoring requirements. Individual permits are issued to facilities with processes or wastewater/stormwater flows that merit unique monitoring requirements. The loading analysis for permitted direct discharges focused on all Individual Permits, GEN15A General Permits, and GEN13 General Permits.[9] All active NPDES permits inside the study area were located using DEQ's Facility Profiler 2.0[10] and the DEQ Wastewater Permits Database.[11] Permitted facilities located within one-half mile of the riverbank between RM 1.9 and 11.8 were sought and compiled using the Facility Profiler and the Wastewater Permits Database. The search revealed 84 NPDES stormwater-permitted (not including construction permits) and 30 NPDES wastewater-permitted discharges to the study area. Of these permitted facilities, 14 are current wastewater-discharge-permitted facilities with either Individual or GEN 15A permits.

For these facilities, the NPDES permits, as well as the most recent two years of Discharge Monitoring Reports (DMRs) for these permits, were assembled from information provided by DEQ on June 3, 2008.[12] From these permits and DMRs, water contaminant concentration data and discharge/flow data were compiled for each facility. These data were available for 10 of the 14 relevant NPDES-permitted discharges:

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[9] Per DEQ (DEQ personal communication 2008), GEN 13 permits were discontinued in 2006; therefore, there are no current GEN 13 permits to include in this analysis. Activities covered under the GEN13 permit (oily stormwater) were subsequently included under the GEN12Z general stormwater permit. GEN 12Z permits are not included in this loading term.

[10] DEQ's Facility Profiler 2.0: (http://deq12.deq.state.or.us/fp20/)

[11] DEQ Wastewater Permits Database: (http://www.deq.state.or.us/wq/sisdata/sisdata.asp)

[12] Information for the Pinnacle Condominium Complex was provided on June 2, 2009.

- Evraz Oregon Steel Mills (EOSM)

- Kinder Morgan/Portland Bulk Terminal 4

- Koppers Inc.

- Starlink Logistics, Inc.

- Siltronic Corporation

- ARCO Products Company

- Kinder Morgan Liquid Terminals

- Equilon Enterprises

- Pinnacle Condominium Complex

- Univar USA.

The remaining four NPDES wastewater-permitted discharges listed below were not included in the loading calculations due to insufficient data for calculations.

Facilities and the reasons they were not included are

- Ash Grove – No flow or contaminant data reported

- Columbia River Sand and Gravel – No flow data reported and no contaminant analysis required (only TSS and turbidity monitored)

- Vigor (Cascade General) – No flow data reported on DMRs

- Hoyt Street Properties – No flow or concentration data reported.

The discharge information from these sites would be expected to increase the upper and lower end estimates of total loading to the study area for the contaminants included in their permits. The lack of data for these facilities is not expected to represent a significant loading data gap for any parameters.

E4.2   APPROACH

The information described above was gathered into an Excel database, including information on each outfall regulated by each of the permits. (Note: One facility permit may regulate multiple outfalls, generating multiple DMRs.) The database compiled all contaminant concentration information, as well as discharge information, in chronological order, including all available monthly and quarterly records. This database was used to estimate annual loads, based on the product of reported monthly or quarterly discharge rates and contaminant concentrations.

For each permitted discharging facility, a range of annual contaminant loading was estimated, as described below.

E4.2.1   Load Estimates from DMRs

Total monthly discharge volume and contaminant concentration data, for select reported contaminants, was reported monthly on DMRs for all facilities except ARCO and Pinnacle. For these two facilities, discharge volume and contaminant concentration data are reported on a quarterly basis. For the Starlink facility, metals are reported on a monthly basis, while DDT is reported quarterly. The method for calculating average annual loading for DMRs submitted monthly is shown below.

For each facility, a total monthly load was calculated for each month of the most recent two years of data using the following equation:

$$L_{monthly}\left(kg\middle/month\right) = C_{monthly}\left(mg\middle/L\right) \times Q_{monthly}\left(L\middle/month\right) \times 10^{-6}\left(kg\middle/mg\right)$$

Where:

$L_{monthly}$ = monthly load
$C_{monthly}$ = single monthly concentration measurement reported in DMR
$Q_{monthly}$ = single monthly discharge volume.[13]

The total annual load for each of the most recent two years was then calculated from monthly loads by summing the twelve calculated monthly loads:

$$L_{annual\_1}\left(kg\middle/yr\right) = \sum L_{monthly\_1}\left(kg\middle/month\right)$$

$$L_{annual\_2}\left(kg\middle/yr\right) = \sum L_{monthly\_2}\left(kg\middle/month\right)$$

Where:

L_{annual_1} = average annual load, year 1
L_{annual_2} = average annual load, year 2.

Finally, a range of annual loads was estimated by taking the minimum, average, and maximum values of the estimated annual loads (L_{annual_1} and L_{annual_2}) for the most recent two years.

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[13] Total monthly discharge data were available for Koppers and Starlink. DMRs for other facilities reported a single daily flow volume. Daily flows were multiplied by the total number of days in the month to estimate $Q_{monthly}$. For Kinder Morgan Terminal 4, total monthly volume was estimated based on the reported average flow of 6 cfs because no individual daily or monthly flow measurements were provided in the DMRs. The same approach was applied to generate quarterly flow volume estimates from daily measurements for the ARCO and Pinnacle facilities.

Loads for the following seven permitted dischargers were calculated using monthly monitoring data: Univar, EOSM, Kinder Morgan/Portland Bulk Terminal 4, Koppers, Siltronic, Starlink, and Kinder Morgan Liquid Terminal.

The same general approach was applied for the ARCO and Pinnacle facility data and for Starlink DDT data, which are submitted quarterly: total quarterly loads were estimated and summed to generate total annual loads for the most recent two years. A range of annual loads was estimated by taking the minimum, average, and maximum values of the estimated annual loads.

The resulting DMR-based estimates of lower, upper, and central annual contaminant loading for each contaminant are reported in Table E4-1.

E4.3   PERMITTED POINT SOURCE DISCHARGE LOADING RESULTS

DMR-based loading estimates for each contaminant were summed for all facilities to generate the range of annual loading estimates to the study area by permitted wastewater discharges. Due to limited analyte lists in the DMRs and the permits, data for some contaminant-list parameters were not available for all facilities. Additionally, several contaminants were never monitored at any of the facilities. These results are presented in Table E4-1 for the subset of contaminants for which data were available.

E5.0 ATMOSPHERIC DEPOSITION LOADING ESTIMATES

Atmospheric deposition is a potential source term for loading of contaminants to the study area. This section presents the analysis performed to generate semi-quantitative air deposition loading estimates, including the detailed approach, data sources, results, and a discussion of uncertainty. Air deposition to land, which could subsequently be transported to the river via stormwater runoff, is not included in this analysis and is considered as part of the stormwater analysis. Additional literature information about the mechanism of atmospheric loading can be found in a variety of references including Wesley and Hicks (2000), Seinfeld and Pandis (1998), Bidleman (1988), and USEPA (2005a).

E5.1 APPROACH

Atmospheric deposition represents the sum of both dry and wet deposition. When there is no precipitation, gases and particles are deposited to the ground surface in a process known as dry deposition. During precipitation events, gases and particles can be scavenged by rain droplets, frozen precipitation elements (freezing rain or snow), or fog droplets that deposit to the surface, a process known as wet deposition. The following subsections present the details of the approach applied to assess dry, wet, and total deposition loading to the study area.

E5.1.1 Dry Deposition

The flux to a surface from dry deposition can be estimated as (Seinfeld and Pandis 1998; Reinfelder et al. 2004; note that unit conversions are necessary to ensure dimensional consistency):

$$F_i = C_i \cdot v_{d,i} \cdot A$$

Where:

F_i = the mass loading to the surface (kg/y) for species i
C_i = the air concentration of chemical i ($\mu g/m^3$) measured at some reference height from the depositing surface
$v_{d,i}$ = the deposition velocity (cm/s^1) for species i
A = the surface area (m^2)

The deposition velocity term defines the fundamental processes that transport a chemical to the surface. The rate at which a chemical is deposited depends on the level of atmospheric turbulence, chemical properties of the depositing species (molecular diffusivity, water solubility, and vapor pressure), and properties of the surface. Gases may absorb reversibly or irreversibly to the surface; the same is true for chemicals loosely absorbed to particles. Particles—and thus chemicals sorbed to particles—will adhere to the surface; particles deposited to water will be subject to the general processes affecting suspended solids.

Of the three terms used in the calculation of mass flux to the study area surface—surface area, deposition velocity, and concentration—the surface area is known with the greatest certainty and has the smallest temporal variability (varies only a few percent at most with seasonal flow rates and tidal changes; typical value from GIS analysis = 94,633,454 ft^2).

Because of the number and complexity of the physical and chemical processes embedded in the deposition velocity parameter, this term can be difficult to specify properly (Seinfeld and Pandis 1998). Dry deposition velocity for the study area calculations was assigned based on findings from Zufall et al. (1998), who in their evaluation of data from the New Jersey Air Deposition Network (NJADN)[14] showed that dry deposition of particulate matter is dominated by relatively large particles, even though atmospheric particle size distributions are dominated by particles less than 1 µm mass median diameter. The NJADN study selected a value of 0.5 cm/s for dry deposition velocity to reflect the disproportional influence of larger particles in dry deposition, especially in urbanized and industrialized regions (Reinfelder et al. 2004; Franz et al. 1998). Considering the similar urban environment and meteorological conditions between the study area and the NJADN site, a dry deposition velocity of 0.5 cm/s was chosen for calculating dry deposition loading.

Atmospheric concentrations of contaminants are also difficult to specify as they can vary temporally and spatially. Concentration can be estimated through direct measurements or numerical models, both of which have associated uncertainties. The data sources applied to assign atmospheric concentrations of contaminants are discussed in Section E5.2.

The general approach used in this analysis to estimate mass flux to the study area is to capture the uncertainty and variability of both the deposition velocity and concentration by employing a range of estimates for each parameter. For dry deposition, the upper-bound estimates of deposition velocity and concentration are combined to provide an upper-bound estimate of mass flux; an analogous procedure is used to provide a lower-bound mass flux estimate. Given the uncertainty and variability inherent in each of the input parameters, where a central estimate can be provided, this estimate is uncertain at least within the upper- and lower-bound ranges presented.

E5.1.2   Wet Deposition

For certain analytes, wet deposition can be an important term in total atmospheric loading. Three fundamental steps describe the wet deposition process: 1) transport of the species (gas or particle) to the precipitation element; 2) uptake (or "scavenging") of the species by the precipitation element; and 3) delivery of the species to the Earth's surface. Accurate determination of wet deposition flux is significantly more challenging than dry deposition flux for several reasons. Almost all of these processes can be reversible. For

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[14] The NJADN was established in late 1997 as a research and air monitoring network (1) to characterize the regional atmospheric levels of hazardous air pollutants, (2) to estimate atmospheric loadings to aquatic and terrestrial ecosystems, (3) to identify and quantify regional versus local sources and sinks, and (4) to identify environmental variables controlling atmospheric concentrations of PCBs, PAHs, chlorinated pesticides, trace metals, mercury, and nutrients.

instance, particles scavenged by rain droplets may be re-aerosolized by evaporation of the rain droplet during its descent to the Earth. These processes occur across a large of physical scales (from oxidation/reduction [redox] reactions within rain droplets to macroscale processes such as synoptic weather). The presence of multiple phases of both precipitation elements and chemicals can affect the rate of uptake by a precipitation element by orders of magnitude (Poster and Baker 1996). Finally, the size of particulate analytes and precipitation elements greatly influences the rate of precipitation scavenging.

The most reliable way available to estimate wet deposition is to collect all precipitation in suitable samplers, measure the contaminant concentrations, and calculate the daily wet deposition flux in the sampling period (Reinfelder et al. 2004):

$$Flux_{wet} = C_{precip} \cdot PI$$

Where:

$Flux_{wet}$ = the wet deposition flux ($\mu g/m^2/day$)
C_{precip} = the contaminant-specific concentration in the precipitation sample ($\mu g/m^3$)
PI = the precipitation intensity (m/day).

For seasonal and annual wet deposition flux, volume-weighted mean concentration, which is calculated by total mass of contaminant divided by total precipitation volume, should be used as concentration in precipitation. Subsequently, the total annual wet deposition loading (kg/year) is calculated by multiplying the volume-weighted mean concentration ($\mu g/m^3$) by the area of interest (m^2) and by the total annual deposition (m/year), plus by the unit conversion factor (10^{-9} kg/μg).

Study area-specific wet deposition monitoring results are only available for total PCBs for 2007 (MWH 2008) and mercury (Hope 2005). Wet deposition estimates for PCBs were calculated as described above using data collected by MWH Americas, Inc. during May to June 2007. For mercury, findings from Hope (2005) were considered for comparison with estimates based on NJADN data (see next paragraph). Briefly, the Hope (2005) study used precipitation monitoring data from Oregon Mercury Deposition Network sites (one site near Beaverton and one site near the southern end of the basin), and found wet deposition estimates comparable to those generated by the NJADN ratio approach, as described below.[15]

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[15] Hope (2005) calculated dry, wet, and total mercury loading rates to surface water for the entire Willamette River basin (398,000,000 m^2). When scaled down to the sub-area of the basin represented by the study area (8,791,735 m^2, 2 percent of the open water area estimated by Hope), Hope estimates a total atmospheric mercury load of 0.08 kg/yr. This result is slight lower than, but comparable to, the lower mercury load (0.11 kg/yr) presented here.

Values were estimated by calculation for those contaminants that lack study area-specific monitoring results,. An NJADN study by Reinfelder et al. (2004) showed that the wet deposition flux can be estimated from 1) the total atmospheric concentration, 2) the fraction of the contaminant present in the particulate-associated and gaseous phases, 3) the precipitation intensity, 4) the Henry's Law constant, and 5) the particle scavenging coefficient. The following equations were applied to estimate loads to the study area based on monitoring results from NJADN (Reinfelder et al. 2004), with correction by ratios[16] to study area total atmospheric concentrations and total annual precipitation.

$$WDep = WDep_{NJADN} \cdot f_{Conc} \cdot f_{Precip}$$

$$f_{Conc} = Ci_{SA}/Ci_{Jersey\ City}$$

$$f_{Precip} = P_{Portland}/P_{Jersey\ City} = 0.88$$

Where:

$WDep$	=	wet deposition loading to the study area (kg/year)
$WDep_{NJADN}$	=	wet deposition loading collected by NJADN (kg/year)
f_{Conc}	=	atmospheric concentration correction factor
f_{Precip}	=	annual precipitation factor
Ci_{SA}	=	atmospheric contaminant concentration for contaminant i in the study area ($\mu g/m^3$)
$Ci_{Jersey\ City}$	=	atmospheric contaminant concentration for contaminant i in Jersey City ($\mu g/m^3$)
$P_{Portland}$	=	annual precipitation in Portland (based on 30 year average; inch/year)
$P_{Jersey\ City}$	=	annual precipitation in Jersey City (based on 30 year average; inch/year).

(Please note that unit conversions are necessary to ensure dimensional consistency.)

E5.1.3   Total Deposition

For each contaminant, the central estimate of total deposition loading to the study area was estimated by summing the dry deposition loading and the wet deposition loading estimates, where available. Because only central estimates could be generated for wet deposition loading, upper and lower estimates of the total loads were based on an assumption of that the ratio between the central wet and dry estimates was consistent across the range. Specifically, the ratio of the central estimate for wet deposition to the central estimate for dry deposition was calculated and assumed to be representative of the wet:dry ratios for the upper and lower values. From this ratio, upper and lower wet

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[16] Because the wet deposition flux is proportional to the atmospheric concentration and precipitation intensity, the two correction factors convert the NJADN monitoring results to be study area-specific.

deposition values were estimated and included in the range of estimates for total deposition. Total loading estimates reflect summing of these ratio-estimated wet deposition load estimates for the lower and upper estimates. Where wet deposition data were inadequate to allow for estimation of even a central estimate, total loads were assigned based on the dry deposition estimates, and the lack of wet deposition contribution to the estimate is noted.

E5.2   DATA SOURCES

In an effort to collect atmospheric deposition and air sampling and monitoring data, a wide range of databases were reviewed for pertinent data related to the Lower Willamette River study area, including the following:

- Agency for Toxic Substances and Disease Registry online toxicological profile records (ATSDR 2008)

- California Ambient Dioxin Air Monitoring Program (CADAMP; CARB 2004)

- USEPA AIRS (Aerometric Information Retrieval System; USEPA 2008b)

- USEPA Interagency Monitoring of Protected Visual Environments (IMPROVE; USFS 2008)

- USEPA NADP (National Air Deposition Program; USEPA 2008d)

- USEPA Clean Air Status and Trends Network (CASTnet; EPA 2008c)

- USEPA Mercury Deposition Network (MDN; USEPA 2008d)

- USEPA National Air Toxics Assessment (NATA) Modeled Ambient Concentrations (USEPA 1996)

- USEPA NATA Monitored Ambient Concentrations (USEPA 2008a)

- USEPA National Dioxin Air Monitoring Network (NDAMN; USEPA 2008e)

- MWH Americas, Inc. (MWH 2008)

- National Park Service monitoring networks (NPS 2008)

- New Jersey Atmospheric Deposition Network (Reinfelder et al. 2004)

- Oregon DEQ all data sources including Laboratory Analytical Storage and Retrieval (LASAR; DEQ 2006)

- Oregon Mercury Deposition Network sites (one site near Beaverton and one site near the southern end of the basin), as reported in Hope (2005).

Based on this review of available atmospheric data, the following data sources were used:

- LASAR,

- NJADN,

- USEPA NATA modeled and monitored ambient concentrations,

- CADAMP,

- MWH Americas,

- Oregon Mercury Deposition Network (as reported in Hope 2005), and

- ATSDR (2002a, 2002b).

Portland-specific data were available from the LASAR database and MWH Americas, Inc. In all, data from seven LASAR stations were used in these calculations. Each station identification number was then used as a primary parameter for data querying. Of the contaminants listed in Table 6.0-1, only data for seven metals (arsenic, chromium, copper, lead, mercury, nickel, and zinc) and two PAH analytes (BaP and naphthalene) were available from this local empirical data source.[17] study area-specific wet deposition monitoring results for total PCBs were obtained from MWH Americas, Inc. (MWH 2008). The remaining information was collected from the other sources noted. Data and data sources for dry deposition air concentrations and wet deposition flux rates used in loading calculations are presented in Tables E5-1a and E5-1b, respectively.

For PAHs, empirical non-local air concentration data were available through the NJADN database. Local modeled NATA results were also available. To select the most appropriate data set, the direct monitoring results for total PAHs (the sum of the 13 site PAHs for which data was available) in the New Jersey NJADN database were compared to the NATA modeled ambient concentrations for total PAHs (the sum of 16 site PAHs) for Washington County and Multnomah County. This comparison found that the NATA modeled ambient concentrations were 2 to 4 orders of magnitude higher than the measured New Jersey data. Based on the statistical evaluations, it is determined that the total of 13 PAHs from NJADN is a better representative value for the atmospheric deposition loading calculations than the total of 16 PAHs values reported by NATA, and the NATA total PAH data were excluded from atmospheric loading calculations. For other contaminants (hexachlorobenzene, TCDD TEQ) the modeled NATA data were the

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[17] Individual high-concentration samples were observed for both BaP and naphthalene in the LASAR data. These high samples were collected on a specific sampling date at the monitoring location in the urban area of Portland near two major roads. The reported concentrations for these two chemicals are at least 2 orders of magnitude higher than the next highest monitoring values in the LASAR data set. To ensure the representativeness of these monitoring data values for BaP and naphthalene for applications to atmospheric deposition loading calculations, a thorough statistical analysis of the LASAR data was performed. The statistical analysis showed that among the reported monitoring data for BaP, a maximum value of 0.32 µg/m^3 and an average value of 0.19 µg/m^3 are outliers; therefore, they are excluded from the atmospheric loading calculations. For naphthalene, the following values determined to be statistical outliers also were excluded from the atmospheric loading calculations: 2.16 µg/m^3 as one of the maximum values, 1.87 µg/m^3 as an average value, and 1.55 µg/m^3 as a minimum value from the LASAR database.

only air concentration data available; in these cases the NATA data were used in the atmospheric deposition loading calculations.

For a number of contaminants—individual PCB congeners, total PCDD/Fs, 4,4´-DDD, total DDD, total DDE, total DDT, BEHP, total petroleum hydrocarbons and total petroleum hydrocarbons (residual), pentachlorophenol, gamma-hexachlorocyclohexane (Lindane), and tributyltin ion—no measured or modeled concentrations or wet deposition estimates were available. Therefore, no estimates of atmospheric deposition loading are provided for these contaminants.

E5.3   ATMOSPHERIC DEPOSITION LOADING RESULTS

Table E5-2 presents the estimates of atmospheric dry deposition loading, wet deposition loading, and total deposition loading to the study area water surface. For the majority of the analytes, Table E5-2 provides lower, central, and upper tendency estimates of dry deposition loading; however, due to data limitations, only central tendency estimates could be generated for wet deposition loading. These results are discussed in Section 6.1.4.

E5.4   UNCERTAINTY

Primarily due to the limited availability of local atmospheric concentration and precipitation concentration monitoring data, atmospheric deposition to the river surface is expected to be one of the most uncertain loading terms. In the case of the atmospheric deposition loading estimates, the presented range of estimates (lower, central, upper) is not expected to fully capture/represent the uncertainty associated with this term, due to significantly limited local empirical data.

For dry deposition loading estimates, the major uncertainties are as follows:

- The limited available local atmospheric concentration data

- The necessarily simplified calculation methodology

- The uncertainty associated with selection and uniform application of a deposition velocity.

For wet deposition loading estimates, the major uncertainties are as follows:

- The extremely limited local wet deposition monitoring data (data only found for PCBs [only a partial year of sampling record available] and mercury)

- The uncertainty associated with application of precipitation correction factors to allow for use of NJADN data.

Finally, because the total deposition loading was estimated by combining the dry and wet deposition loading, the identified uncertainties associated with dry and wet deposition loading are also relevant to the estimated total deposition loading.

E6.0 GROUNDWATER LOADING ESTIMATES

E6.1   UPLAND GROUNDWATER PLUME LOADING ESTIMATES

This section presents the detailed approach, calculations, and results for the upland groundwater plume loading estimates. For each of the nine GWPA study sites (see Appendix C2 for detailed discussion of site selection and GWPA data interpretation), groundwater contaminant loads to surface water were calculated to generate a range of annual loading estimates from upland groundwater plumes to surface water at the scale of the study area and for the individual study sites.

These groundwater plume loading estimates are based on empirical information from only nine study sites, and it is possible that other sites will be identified that have a complete pathway for upland groundwater plumes to the study area. The groundwater pathway site selection process was designed to identify all sites with a reasonable likelihood of exhibiting a complete transport pathway for upland groundwater plumes to the study area. As described in Appendix C2, 83 sites lacked sufficient data to determine the completeness of the groundwater pathway. There may be additional upland sites that lack groundwater data but have complete groundwater pathways.

These estimates assume that observed transition zone water (TZW) concentrations are entirely attributable to upland groundwater. In some cases, the only likely pathway for a contaminant to enter the transition zone is via the groundwater pathway, originating from upland groundwater plumes. Loading estimates for such conditions are expected to be reasonably good approximations of mass loading from groundwater plumes to surface water. Where in-river sediment contamination may be a source of contaminants detected in surface water, the groundwater plume loading estimates may be partially redundant with advective loading estimates, described below in Section E6.2.

E6.1.1   Data Sources

Data collected as part of the LWG Round 2 Groundwater Pathway Assessment, the Siltronic offshore investigation (MFA 2005; Hahn and Associates 2005) and the Gasco Offshore Investigation (Anchor 2008) were used to generate these plume loading estimates. Three types of information were used:

1. Measured TZW contaminant concentrations from 150 sample locations at the nine study sites were used to estimate contaminant concentrations. These samples represent the complete data set for the sample depth interval from 0 to 38 cm below mud line (bml)[18] (see Maps 2.1-20a-l). The sampling methods included in

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[18] In 2007, on behalf of Gasco, Anchor Environmental conducted an investigation of the groundwater pathway offshore of the Gasco site. Twenty-two TZW samples were collected with a Geoprobe sampler at depths between 0 and 90 cm bml. Samples collected from 0 to 38 bml were not available for this data set; therefore, all samples from the 0 to 90 cm bml interval are included in the groundwater plume loading data set. These data are presented in detail in Anchor (2008) and discussed in Appendix C2.

this data set are small-volume peepers, Trident, and Geoprobe. Both unfiltered and filtered (where available) results were evaluated.

2. Seventy-seven flow-meter measurements (24 hour, 15-minute interval records from ultrasonic seepage meters capable of positive and negative readings) were used to estimate groundwater flux within 29 flow zone areas identified at the nine study sites. The 24-hour maximum and average seepage rates are presented spatially on Figures E6-1 through E6-7. In the design of the TZW study (Integral 2004), seepage meters were purposefully placed at locations where there was an indication (based on Trident temperature measurements, sediment texture, or screening results) of higher flow rates. These flow-meter measurements are presented in Appendix C2.

3. Twenty-nine site-specific flow zone areas generated from interpretation of multiple lines of evidence, including TZW chemistry results, seepage meter data, discharge mapping temperature data, sediment textures, sediment chemistry, and upland stratigraphy, were used to group analytical and flow data sets for the calculations. These flow zones are presented with discussions supporting the interpretations in Appendix C2. The flow zones are also presented in this appendix in support of the approach discussion that follows.

E6.1.2 Approach

Groundwater plume contaminant loads to surface water were estimated based on observed TZW contaminant concentrations and seepage meter flow rates. Loading was estimated for each flow zone area offshore of each TZW study site. The approach to estimating concentrations and flow rates within each flow zone, then compiling the information to calculate annual loads, is presented in the following sections.

E6.1.2.1 TZW Concentrations

TZW sample data from the sample depth interval from 0 to 38 cm bml were used as the concentration terms in the loading calculations. These data were assigned to flow zones based on sample location. For flow zones with only one TZW sample, the concentration was applied to the entire zone. Thiessen polygons were developed around each TZW sample location within flow zones containing multiple TZW samples. The concentration of each sample was then applied to the corresponding partial area of the flow zone. The flow zones, TZW sample locations, and corresponding Thiessen polygons are presented in Figures E6-1 through E6-7.

In a small number of cases, more than one TZW sample was collected at a single location for a given analyte. For these collocated samples, the maximum observed concentration was used in the calculations. Contaminant concentrations below laboratory-reported analytical detection limits were assigned a value of zero, in accordance with the approach for all RI loading calculations. Additionally, TZW samples were not analyzed for all target analytes at all sampling locations due to occasional limits in sample volume. Within individual Thiessen polygons within a flow zone lacking data for a particular targeted contaminant, the contaminant concentration was estimated as the average of all

other concentrations measured in the same flow zone. Finally, if an analyte was not sampled offshore of a given upland site, loading estimates for the flow zones associated with that site were not generated.

Calculations were performed with both unfiltered and filtered data sets.[19] The unfiltered data set consisted of unfiltered push probe (Trident and Geoprobe) samples, as well as small-volume peeper samples. The filtered data set consisted of the available 0.45-µm filtered push probe sampling results and the small-volume peeper results (the small-volume peeper results were used for both the filtered and unfiltered estimates). Because of sample volume limitations, filtered contaminant concentrations were not collected for all analytes at all locations. Therefore, at locations where filtered samples were not collected, the average of the filtered push probe contaminant concentrations within the same flow zone was used as a proxy value to complete the data set needed for the filtered load estimates.

Three flow zones covered areas that did not include any TZW sample locations. Contaminant concentrations for these flow zones were estimated based on nearby TZW measurements. In particular, for the nearshore ARCO groundwater discharge zone (area = 1,900 ft^2; see Figure E6-2) the nearest TZW sample (R2-AR-02) was used. No concentration data were available for the Rhone Poulenc inferred groundwater discharge zone extension (area = 55,000 ft^2; see Figure E6-4); therefore, the contaminant concentrations were estimated as the average concentrations of all Rhone Poulenc groundwater discharge zone samples. Finally, for the Willbridge Terminal low-to-no groundwater discharge zone (area = 780,000 ft^2; see Figure E6-6), the average contaminant concentrations from the lower flow rate groundwater discharge zone were used.

E6.1.2.2   Groundwater Discharge Flow Rates

In each flow zone, loads were calculated for minimum, mean, and maximum groundwater flow rates to produce a range of loading estimates. The lower, central, and upper estimates of seepage flux rates for each flow zone (q_{lower}, $q_{central}$, and q_{upper}, in units of cm/day) were assigned based on the range of observed daily flux at each seepage meter within each zone. Seepage meter locations with negative average seepage rates (representing net recharge from the river to the groundwater) were included in the calculation of $q_{central}$ for each flow zone as a flux of 0 cm/d; however, the minimum q_{lower} estimate applied was 0.1 cm/day, recognizing the measurement accuracy of the Ultraseep seepage meters used in the study. Of the 29 flow zones identified offshore of the nine study sites, five did not include direct seepage meter measurements. Flow rates were applied to these five zones using professional judgment, based on flows in similar or adjacent zones.

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[19] Following sample collection protocols, filtered samples of VOCs and naphthalene were not collected. For these analytes, filtered loading estimates were not generated.

Lower, central, and upper estimated seepage flux rates (q_{lower}, $q_{central}$, and q_{upper}) were converted to annual flow rates (Q_{lower}, $Q_{central}$, and Q_{upper} in ft^3/year) for each sample polygon area, according to the following equation:

$$Q \ (ft^3/year) = q \ (cm/day) \times A \ (ft^2) \times 0.03281(ft/cm) \times 365 \ (day/year).$$

Table E6-1 summarizes sample polygon areas, mean and maximum groundwater flow rates, and calculated groundwater discharge volumes.

E6.1.2.3   Upland Groundwater Plume Loading

Loading estimates were prepared for each polygon as the product of the flow rate and the concentration. Loading rates for each flow zone area were estimated by summing the estimated loads for each of the sample polygons within the flow zone, using the following general equation:

$$Load_{flowzone} = \Sigma(C_{sample} \ x \ A_{sample} \ x \ UnitFluxRate)$$

Where:

$Load_{flowzone}$	=	the estimated annual mass loading to surface water, in units of mass per time
C_{sample}	=	the contaminant concentration the TZW
A_{sample}	=	the area of the Thiessen polygon associated with the given sample
UnitFluxRate	=	measured groundwater-to-surface water seepage flux rate.

A range of loading estimates for each flow zone was determined by applying both the filtered and unfiltered concentrations to the calculations as well as the minimum, mean, and maximum measured seepage flux rates for the given flow zone. From the resulting six estimates, the range was determined by the central unfiltered estimate (upper load), the central filtered estimate (central load), and the minimum filtered estimate (lower load). The ranges of loading estimates for the study area were, in turn, generated by summing the estimates for each of the nine study sites.

E6.1.3   Upland Groundwater Plume Loading Results

The estimated ranges of upland groundwater plume annual loading offshore of individual sites, as well as at the study area scale (sum of all nine study sites), are presented in Table E6-2. Based on the calculations described above, a range of lower, central, and upper loading estimates for each analyte were generated for the minimum, mean, and maximum flow rate conditions for both filtered and unfiltered data.

E6.1.4   Uncertainty

The following sources of uncertainty are acknowledged in the upland groundwater plume loading estimates:

- The spatial resolution of the analysis is limited to the resolution of the sampling data sets, as reflected in the Thiessen polygon approach.

- There is no attempt made in these estimates to distinguish the origin of the contaminants in the TZW, and it is expected that the empirical TZW data set includes contaminants originating from sediment contamination (as assessed in the advective loading analysis in Section E6.2 of this appendix).

- The Groundwater Pathway Assessment study design specifically targeted areas of higher seepage and higher TZW concentrations for sampling in the areas offshore of the study sites.

- The TZW concentration estimates do not account for any additional contaminant attenuation to sediments that may occur in the upper 38 cm bml.

- This assessment does not include loading from sites other than the nine study sites that may be discharging upland groundwater plume contaminants to the study area. As described in the site selection process (Appendix C2), the possibility that complete groundwater pathways will be identified in the future at other sites is acknowledged.

- Sampling was conducted during the hydrologic season of high expected groundwater flow rates to maximize the observed groundwater signal (plume concentration and flow rate). Consequently, the lower end of the groundwater signal in the discharge areas is not captured in the empirical data set.

E6.2 GROUNDWATER DISCHARGE ADVECTIVE LOADING ESTIMATES

This section presents the estimation of loading of selected contaminants by the mechanism of groundwater advection through contaminated sediments. For the purposes of this analysis, groundwater advective loading is defined as the load resulting from chemicals partitioning from sediment solids into the dissolved phase, then migrating via groundwater advection to the surface sediments. Two advective loading terms are assessed in this section: 1) subsurface sediment advective loading, the loading from subsurface sediment (>30 cm bml) to surface sediment (<30 cm bml) via groundwater advection, and 2) surface sediment advective loading, the transport of contaminants from surface sediment (<30 cm bml) to surface water via groundwater advection. The former is assessed as an external loading mechanism to the Site, and the latter is assessed as a transport process within the study area. Because of the similar assumptions and approach taken to assess these terms, the calculation details are presented together in this section.

E6.2.1 Approach

Advective loads were estimated by first estimating pore water concentrations under an assumption of equilibrium, then applying an estimated groundwater advection rate to generate a mass loading estimate. The rate of contaminant accumulation in surface sediment was estimated from the unit advective loading estimates. These calculations assume a condition of equilibrium in the sediment-pore water environment in all places at all times, and also assume a uniform rate of groundwater advection through all sediments.

While this assumption does not reflect the heterogeneous nature of the study area, both of these assumptions are considered necessary to allow for development of semi-quantitative loading.

Observed sediment concentrations form the basis for estimating pore water concentrations used in both surface and subsurface advective loading estimates. Prior to any calculations, Thiessen polygons were generated (with one polygon representing each sample) for each contaminant from the surface and subsurface sediment data set described in Section E6.2.2.1. A merged polygon set was generated by overlaying and combining the surface and subsurface polygon layers, resulting in a set of polygons each with a single subsurface and surface concentration to support calculations. Calculations were performed for each polygon and summed to generate river-mile and study area-wide estimates.

E6.2.1.1   Pore Water Concentration Estimates

As described above, an assumption of equilibrium was made to estimate pore water concentration (C_{TZW}) from sediment concentration (C_{sed}). Pore water concentrations were estimated for organic contaminants from sediment concentrations using the organic-carbon partitioning coefficient (K_{oc}), and the fraction of organic carbon in the sediments (f_{oc}) as follows:

$$C_{sed} = K_{oc} f_{oc} C_{TZW}$$

Partitioning behavior of metals is described by K_d, and pore water concentrations were estimated from sediment concentrations using the following expression:

$$C_{sed} = K_d C_{TZW}$$

Concentrations measured in sediments are bulk concentrations – they include both the contaminant mass associated with sediment and the mass associated with pore water in the overall sample. As a result, the measured bulk concentrations must be corrected to generate the sediment concentration (C_{sed}). This calculation requires the C_{TZW} value; therefore, an assumption of equilibrium is made in this step. The following equation relates the bulk sediment concentration to the concentration in the pore water and sediment (this equation is the same for both metal and organic contaminants):

$$C_{bulk} = C_{sed} \ x \ \frac{\%solids}{100} + C_{TZW} \ x \left(1 - \frac{\%solids}{100}\right)$$

Replacing the C_{sed} term with the appropriate equilibrium partitioning relationship and solving for C_{TZW} produces the following equation for estimated pore water concentration for organic contaminants:

$$C_{TZW} = \frac{C_{bulk}}{1 + \left(K_{oc} \, x f_{oc} \, \text{-}1 \,) \, x \, \dfrac{\%solids}{100} \right)}$$

For metal contaminants the following equation is generated by the same replacement step:

$$C_{TZW} = \frac{C_{bulk}}{1 + (K_d - 1)\dfrac{\% solids}{100}}$$

E6.2.1.2   Groundwater Advection Rate Estimates

The groundwater discharge rate estimate was generated by applying upland hydrogeologic data gathered for the Round 2 Report (Integral et al. 2007), applying Darcy's Law to generate an estimated total discharge rate to the river, and converting that discharge to a flux rate through the river sediment surface.

For the purposes of these loading calculations, groundwater was assumed to discharge uniformly through sediment over the entire study area, although it is known through direct seepage measurements that the groundwater discharge rate does vary spatially throughout the river. Because seepage measurements are not available for most of the study area, this assumption of uniformity is considered a reasonable approximation to support generation of a range of estimates for this loading term.

As part of the process for developing the Round 2 Report (Integral et al. 2007), the upland CSMs and CSM addenda were reviewed to generate the compilation of hydrogeologic information presented in Table E6-3. This table presents the following types of groundwater information gathered from the CSMs for each site:

- Number of wells
- Aquifer units present
- Groundwater flow direction
- Depth to groundwater
- Depth of the aquifer(s)
- Saturated thickness
- Horizontal gradient
- Vertical gradient
- Hydraulic conductivity
- Transmissivity

- Groundwater velocity.

Darcy's Law was used to generate an estimated groundwater discharge rate to the study area from the information gathered from the CSMs. Darcy's Law describes the relationship between groundwater flow rate (Q), the porosity of the medium, as represented by the hydraulic conductivity (K), the hydraulic gradient ($\Delta h/\Delta l$), and the cross-sectional area (A) to the flow:

$$Q = -K \; x \; A \; x \; (\Delta h/\Delta l \;)$$

The unit flux (q) to the river can, in turn, be estimated as $q = Q/A_s$, where A_s is the cross-sectional area of the river sediment surface.

Therefore, to estimate the total groundwater flow rate (Q) to the river, a representative hydraulic conductivity and hydraulic gradient are needed. Additionally, the total cross-sectional area perpendicular to the groundwater flow and the sediment surface area are needed for the entire study area. Based on information presented in Table E6-3, unit flux values were generated for unconsolidated alluvium by multiplying the reported hydraulic conductivity by the reported hydraulic gradient. The resulting unit flux values ranged from 0.003 to 1.92 ft/day. Discarding the lowest and the highest values, the unit flux values ranged from 0.0625 to 0.15 ft/day, with an average of 0.10 ft/day.

The cross-sectional area of flow was assumed to cover both banks of the river over the complete 9.9 miles of the study area. The average saturated thickness was conservatively assumed to be 60 ft (saturated thickness, as reported in Table E6-3 varies from <1 to >60 ft [the full depth of the channel]). Consequently, the cross-sectional area was estimated to be:

9.9 miles *x* 5,280 ft/mile *x* 2 river banks *x* 60 ft = 6.3E6 ft^2.

Multiplying the average unit flux by the total cross-sectional area produces a central estimate of total groundwater flow rate to the study area of 6.3E5 ft^3/day (7.3 cfs), with a lower estimate of 4.5 cfs and upper estimate of 11 cfs, corresponding to the lower and upper ranges of the upland hydraulic conductivity values.

To determine a unit volumetric flux rate of groundwater through the river sediments, the total groundwater discharge to the river must be divided by the area of the sediment surface. This value was approximated by the area of the sediment polygons representing the sediment concentration information over the study area, which is 9.7E7 ft^2. The resulting estimated unit volumetric flux is 2.4 ft/year (0.20 cm/day), with a lower estimate of 1.5ft/year (0.12 cm/day) and an upper estimate of 3.6 ft/year (0.30 cm/day). This range was used to generate the range of loading estimates for the advective loading term.

The estimated groundwater discharge rate used in the advective loading calculations was compared with the flow rates observed by seepage meter measurements[20] as part of the groundwater plume loading estimates. The net discharge rates for flow zones evaluated at the TZW study sites ranged from 0.86 to 2.0 cm/day, with an average of 1.2 cm/day. Comparing these estimates to the range of values estimated for unit discharge for the entire study area reveals that the Darcy's Law estimate range is roughly 15 percent of the unit discharge rate observed with seepage meters in the nearshore groundwater plume discharge areas. The selective placement of these seepage meters explains the disparity between the two ranges. In the design of the TZW study, seepage meters were purposefully placed at locations where there was an indication (based on pore water temperature measurements, sediment texture, or screening results) of higher flow rates. As such, the seepage meter measurements are expected to be biased high relative to an average unit discharge for the entire study area. Overall, the order-of-magnitude agreement between the unit flux rates developed using these two information sources offers confidence in the utility of the Darcy's Law-estimated rates.

E6.2.1.3   Advective Mass Loading Estimates

Advective loading estimates were generated from estimated pore water concentrations and groundwater flux rates for each polygon using the following equation:

$$Load_{polygon} = C_{TZW} \times A_{polygon} \times Q$$

Where:

C_{TZW} = the estimated contaminant concentration in the pore water
$A_{polygon}$ = the area of the polygon
Q = the estimated annual groundwater flux rate.

Loading estimates for the surface sediment advective loading term were generated from these polygon loads by simply summing all of the polygons within the area of focus (river mile or study area). Not all polygons were summed to generate the resulting loading estimate for subsurface advective loading to surface sediments. For contaminants migrating from subsurface pore water to result in increases in surface sediment concentrations, the pore water concentration in the subsurface interval must be greater than that in the surface interval (as estimated by equilibrium partitioning). As such, a comparison of f_{oc}-normalized sediment concentrations was made in the combined surface and subsurface polygon set. All subsurface polygons with f_{oc}-normalized sediment concentrations greater than concentrations in the corresponding surface polygon were included in the summed loading estimate (for individual river miles and for the entire study area). Maps E6-1 and E6-2 indicate the polygon areas where f_{oc}-normalized subsurface sediment concentrations exceed surface sediment concentrations for PCBs,

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[20] The mean flow rates applied to the upland groundwater plume loading calculations were used in this comparison.

total PCDD/Fs, DDx, and total PAHs.[21] Table E6-4 summarizes the percent of the study area over which subsurface advective loading was assessed for each of the sediment advective loading contaminants. All advective mass loading estimates were generated as a range, including upper and lower estimates as well as a central estimate. The variation in these values is the result of application of the upper, lower, and primary equilibrium partitioning values to the calculations for each polygon, as well as application of the range of estimated groundwater advection rates.

The estimation of advective loading of contaminants presented as analytical sums was completed with an additional step to determine the loading associated with each component of the sum. Polygon-by-polygon loads were calculated for each individual chemical, then summed to estimate the total loading. The sum for total PCBs was calculated from chlorination-based homolog or Aroclor groups rather than for individual congeners. This approach for summed contaminants was taken to minimize the error that would be associated with an attempt to represent partitioning behavior of the entire group by a combined range of K_{oc} values.

E6.2.2 Data Sources

The sediment and partitioning coefficient data sources applied to the estimation of annual advective loading are described in the following subsections.

E6.2.2.1 Sediment Data

The RI data sets in the SCRA were the source of sediment concentration, density, and organic carbon content information used in these calculations. Sediment sampling locations at elevations below 13 ft NAVD88 were included in this analysis, in accordance with the definitions for the study area sediment data set. Additionally, all sediment samples from areas that have subsequently been dredged or capped were excluded from the data sets. From this resulting data set, unique Thiessen polygon sets of sediment data were generated for each contaminant for surface sediment data and subsurface sediment data over the entire study area (RM 1.9–11.8).[22]

Surface sediment data were defined as sediment samples with upper and lower depth boundaries within the interval of 0 to 40 cm bml. The highest concentration for the given contaminant was taken as the representative sample for locations with multiple samples within this interval.

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[21] These maps represent multi-component chemicals (PCBs, DDx, PAHs, and PCDD/Fs). The polygons indicated as included in the subsurface loading assessment are those with at least one component of the given chemical group having higher OC-normalized concentration in the subsurface relative to the surface.

[22] In order to provide maximum spatial resolution near the ends of the study area, Thiessen polygons were generated for all samples between RM 0 and 12.5. All Thiessen polygons were then trimmed to the standard study area definition (RM 1.9–11.8). There are a small number of sample locations (2 or less per analyte) that lie just beyond the extent of the study area which are used to populate the remaining portion of the Thiessen polygons within the study area. If the polygon crossed the study area boundary, data from the sample locations just beyond the study area boundary were used to populate the data set.

Subsurface sediments were defined as all samples with an average depth (upper sampling depth plus lower sampling depth, divided by two) greater than 40 cm. At locations with multiple samples fitting this definition, the uppermost sample was designated as the subsurface sample for this analysis. The objective of this was to identify the sediment data set most representative of the sediment concentration immediately below the surface sediment interval. It is presumed that the concentrations in this interval are the best indicator of equilibrium pore water concentrations from the subsurface sediment that are loading to the surface sediment.

Where sediment samples in the surface or subsurface data set had no reported f_{oc} values, they were assigned using spatial overlay and assignment of correlated values from the surface or subsurface total PCBs data set, which contained complete coverage of f_{oc} measurements. Where percent solids values were missing, the maximum percent solids values for the data set was applied to err on the side of generating conservatively high estimates of concentration in pore water. These areas are shown on Maps E6-1 and E6-2. Polygons missing percent solids data consisted of only 5 to 12 percent of the full data set, and this assumption is not expected to result in a significant impact on the final results. Sediment contaminant concentrations reported as non-detect were assigned a value of zero for the purposes of these loading calculations.

Thiessen polygon sets for summed parameters were developed using the concentration of each individual component chemical applied to the Thiessen set individually. The Thiessen polygon set for total PCBs, was generated first based on homolog data, if available (specifically, nine chlorination-based homolog groups were applied), and secondarily based on Aroclors, where homolog data were not available.

E6.2.2.2 Equilibrium Partitioning Coefficients

An assumption of equilibrium was made to estimate pore water concentrations (C_{TZW}) from sediment concentrations (C_{sed}). The approaches taken to compile partitioning coefficients for organic contaminants and metals are described below.

E6.2.2.2.1 Organic Contaminants

Table E6-5 presents the compilation of octanol-water partition coefficients (K_{ow}) and organic carbon partitioning coefficients (K_{oc}) compiled for the estimation of surface and subsurface sediment advective loading. K_{ow} values describe the tendency of a contaminant to partition between octanol and water. K_{oc} values describe the tendency of a contaminant to partition between organic carbon (typically associated with solids) and water. Table E6-5 also presents summaries of primary values and ranges of K_{ow} and K_{oc} applied to the calculations.

A literature search for K_{ow} values was conducted to compile partition coefficients. Ranges of both K_{oc} and K_{ow} values are reported widely in the scientific literature for many of the contaminants to be assessed in the RI sediment advective loading analysis. K_{ow} values for organic contaminants in this analysis were compiled for conversion to K_{oc} values. K_{ow} values were chosen as the basis for K_{oc} values because they exhibit less

inherent variability, as compared to K_{oc} values, since they describe the distribution of a contaminant between two well-defined solutions (octanol and water). In contrast, organic carbon can vary widely in hydrophobicity, functional group content, and resulting partitioning behavior, resulting in a wide range of reported literature values for K_{oc}.

A range of K_{ow} values was compiled for individual organic contaminants from the following sources/tools, in accordance with the USEPA Equilibrium Sediment Benchmarks (USEPA ESB) documents for the protection of benthic organisms (USEPA 2008g [tier 2 non-ionic organics], USEPA 2003c [PAH mixtures]):

1. USEPA ESB documents (USEPA 2003a,b,c)
2. SPARC model[23] V4.2 (http://ibmlc2.chem.uga.edu/sparc) (SPARC 2009)
3. Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals (Mackay et al. 2006)[24]
4. Oak Ridge National Laboratory-Risk Assessment Information System (ORNL-RAIS) database (http://rais.ornl.gov/) (ORNL 2006)
5. ATSDR Toxicological Profiles[25] (http://www.atsdr.cdc.gov/toxpro2.html) (ATSDR 2006)
6. Other literature sources.[26]

Table E6-5 presents the K_{ow} data compiled from each of these sources.

The upper and lower advective loading estimates for this advective loading analysis are based on the maximum and minimum K_{ow} values, respectively, for all of the compiled sources listed above. Prior to selection of the minimum and maximum values, the compiled set of K_{ow} values was analyzed for the presence of high or low outlying values. This analysis involved calculating the logarithm of the K_{ow} values, then plotting log K_{ow} on box-and-whisker plots. Values were identified as outliers on the box-and-whisker

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[23] The SPARC model numerically predicts K_{ow} values, and in addition, the model has a database of experimentally measured values; both values were compiled where available.

[24] Mackay et al. (2006) provide a range of K_{ow} values for many chemicals, as well as a selected value from this range for a subset of chemicals. In loading calculations, the range of K_{ow} values was used to determine the minimum and maximum K_{ow}. The selected value was used as the primary K_{ow} when available. When a selected K_{ow} value was not provided, the geometric mean of the minimum and maximum K_{ow} values was used as the primary K_{ow}.

[25] ATSDR Toxicological Profiles provide a range of K_{ow} values for many chemicals. In loading calculations, the range of K_{ow} value was used to determine the minimum and maximum K_{ow}. The geometric mean of the minimum and maximum K_{ow} values was used as the primary K_{ow}.

[26] For tributyltin ion, Aroclor 1262, and Aroclor 1268, K_{ow} data were not available from the primary sources. The USEPA KowWIN software (USEPA Estimation Program Interface [EPI], http://www.epa.gov/oppt/exposure/pubs/episuite.htm) and the literature source (Arnold et al. 1997) were used to generate K_{ow} values for tributyltin ion. The K_{ow} values for Aroclor 1260 were used in loading calculations for Aroclor 1262 and Aroclor 1268.

plots using standard metrics[27]. Outlying values were excluded from the determination of the minimum and maximum K_{ow} values.

Primary K_{ow} values are used for calculating the central estimates of annual advective loading. These primary values were selected from the compiled data set following the order of preference listed above. Mackay et al. (2006) was considered the preferred reference for PCBs.[28] All primary values for PCBs (congeners, homologs, and Aroclors) were calculated as the geometric mean of the minimum and maximum Mackay et al. (2006) values with outliers excluded.

Ranges of K_{ow} values were compiled from the SPARC model and Mackay et al. (2006) for individual components of those contaminants presented as summed totals. This approach is expected to provide more accurate loading estimates compared to the simple application of a single range of K_{oc} values to a group of chemicals, because many of these chemical groups contain chemicals with a large range of partitioning behavior and associated K_{ow} values. A range of K_{ow} values for the ten isomer homologs was compiled from Mackay et al. (2006) for total PCBs measured as congeners. K_{ow} values for the nine Aroclor groups detected in the study area were also compiled from Mackay et al. (2006) for total PCBs measured as Aroclors

To assess partitioning between water and organic matter in the study area, the K_{ow} values tabulated in Table E6-5 were utilized to calculate K_{oc} values using the equation provided in DiToro et al. (1991):

$$\log_{10} K_{oc} = 0.00028 + \log_{10}K_{ow} \times 0.983$$

The literature contains many K_{ow}-K_{oc} conversion equations (Gawlik et al. [1997] compiled 76 of these relationships). However, USEPA found that the DiToro equation was subject to less uncertainty than other equations (USEPA 2003c). Resulting K_{oc} values are presented in Table E6-5.

E6.2.2.2.2 Metals

Table E6-6 presents a compilation of log K_d values for use in the surface and subsurface sediment advective loading calculations. Because metals partitioning behavior is not simply a hydrophobic mechanism, K_d values must be applied to the equation. Metal partitioning can be strongly affected by solution chemistry (for example, pH, the presence of dissolved ligands such as Cl⁻ or dissolved organic matter, and redox state) and by the characteristics of the sediment itself (for example, the presence of ion-exchange sites on

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[27] The box-and-whisker plots are created such that the central line is the median, and the lower and upper bounds of the box are the 25th and 75th-percentiles. Outliers are defined as values that are greater than the sum of the upper 75th percentile and 1.5 times the inter-quartile range, and less than 25th percentile minus 1.5 times the inter-quartile range.

[28] The use of Mackay and Shiu (2006) as the preferred source for PCB congener K_{ow} values was based on comments from USEPA on the Round 2 Report. Mackay and Shiu (2006) provide tables of K_{ow} for a selection of analytes (e.g., approximately 50 of the PCB congeners); in addition, for each compound included, a compilation of published K_{ow} values is provided.

minerals, the lability of complexation sites on sediment organic matter). These K_d values were selected from an USEPA compilation of metals partitioning coefficients (USEPA 2005b). The K_d values selected are specific for the partitioning of metals between sediment and pore water. This compilation provided both estimates of central tendency (mean and median) and a range of values. For these calculations the mean, minimum, and maximum K_d values were used for generation of the ranges of advective loading estimates.

E6.2.3   Groundwater Discharge Advective Loading Results

Lower, central, and upper range estimates of surface sediment advective annual loading to surface water are presented in Table E6-7 for the entire study area and by river mile for the contaminants evaluated in the sediment advective loading analysis. Lower, central, and upper range estimates of subsurface sediment advective annual loading to surface sediment are presented in Table E6-8 for the entire study area and by river mile. These results are discussed in Section 6.1.6 and in Section 10.

E6.2.4   Uncertainty

There is significant uncertainty associated with the advective loading estimates related to applied assumptions as well as the data sets used in the calculations. The primary uncertainty related to equilibrium is the assumption of equilibrium in all parts of the sediment/pore water environment at all times. This calculation fails to capture the sorption-desorption-resorption dynamics that occur in advective transport through sediment. Beyond the assumption of equilibrium, that the site organic carbon associated with sediments may differ in character from that defined by the range of literature K_{oc} values. Further, this assessment ignores any chemical or biological transformation processes that may occur in the migration process.

There are a number of significant uncertainties related to the groundwater advection annual loading estimates. They are based on the limited available upland data and not on groundwater modeling of the area or direct measurement of seepage rates representative of the entire study area (though they compared reasonably to the limited set of seepage measurements taken in the system). Groundwater advection load estimates rely on a simple and conservatively high cross-sectional area, and apply a projection of the sediment surface area to represent the actual sediment surface area (thereby increasing the unit discharge estimate). Finally, the assumption of a constant discharge rate fails to capture the variability in discharge rates that is expected but not quantified across the study area.

E7.0 RIVERBANK EROSION

No quantitative estimation of the loading of contaminants to the in-water portion of the study area from bank erosion is performed in this RI. The LWG has reviewed multiple sources of information to identify bank soil chemistry data sets. These efforts included review of individual site summaries, summarization of beach and/or bank data collected by the LWG through 2007, and inquiry with DEQ for specific relevant site information. The data found to date are summarized in Table E7-1, and a detailed data flat file compiled for several sites is delivered electronically with this document (Attachment E-3). Map E7-1 presents the bank soil sampling locations sampled to date.

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